RETRACTION OF COLD DRAWN POLYETHYLENE: THE INFLUENCE OF LAMELLAR THICKNESS AND DENSITY

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August 1971

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ABSTRACT

The role of crystal morphology in the retraction of oriented, linear polyethylene was studied utilizing samples crystallized under conditions controlled to vary, separately, lamellar crystal thickness and density. Samples were oriented in a simple shear deformation to a strain of 4.0 prior to measuring retraction tendency in creep and relaxation type tests. Characterizations of specimens were made using wide and small angle Xray techniques. The specific morphological variations were chosen to test the hypothesis that a long range elastic restoring force can originate in conjunction with deformation of lamellar crystals and the consequent increase in lamellar crystal surface area and surface free energy. The results support this hypothesis.

INTRODUCTION

When a crystalline linear high polymer is oriented by mechanical deformation, as in cold-drawing, it retains a tendency to retract or to revert to its underformed state. Heating the specimen above the drawing temperature speeds the retraction and also apparently increases the magnitude of the retraction. At temperatures near the melting point of the polymer, nearly complete recovery from deformation can be observed. This behavior has been known for some time and has been widely attributed to "rubber elasticity" associated with orientation of molecules in the amorphous regions of "semi-crystalline" polymers. While this interpretation may be useful in viewing the response of materials of relatively low crystallinity or materials having an identifiable amorphous phase it is less useful in assessing the behavior of drawn highly crystalline polymers. At least two recent reports suggest that the origin of the retraction tendency may be the deformed lamellar crystals (1, 2). Because the lamellar polymer crystals are small, there is a large amount of crystal surface or crystal interface. Deformation of the crystals increases the surface or interface area thus increasing the free energy of the system and creating the driving force for retraction. This paper reports on experiments performed to obtain a measure of the role of crystal size and crystallinity in the retraction of polyethylene.

SAMPLE CRYSTALLIZATION

Marlex 6050, a linear polyethylene produced by Phillips Petroleum Company was used throughout this study. As part of a previous study (3) using the same lot of polymer, molecular weight determinations were made with the results $\bar{M}n$ = 5500 and $\bar{M}w$ = 92,500. Sheet specimens 4 mm thick were prepared by pressing pellets of

Marlex 6050 in a rectangular mold at 150 C and 130 kg/cm^2. The sheets were then heated to 180 C for 75 minutes and pressed to a thickness of 3.2 mm. At the end of the 75 minutes, the molds were transferred to a silicone oil bath preset to the desired crystallization temperature. After the desired time for crystallization, the mold was quenched by immersion in ice water. Table 1 summarizes data on the crystallization conditions and characterizations of the specimens by density gradient column and small angle Xray diffraction. The SAX data were obtained on a Bonse and Hart type unit. The diffraction scans, after subtraction of diffuse scatter following the procedure of Muzzy (4), are reproduced in Fig. 1. These procedures yielded one set of four specimens with essentially the same density but differing in SAX spacing or lamellar thickness and another set of four specimens with the same SAX spacing but different densities. One specimen was prepared by quenching the mold from 180 C into ice water.

COLD DRAWING OF SAMPLES

High density polyethylene which has been crystallized relatively slowly at high temperatures is difficult to cold-draw in tension; it tends to fracture. For this reason, and because it permits direct control of the strain or draw ratio, a simple shear deformation was used. The sample geometry and the jaws used to perform the shearing is shown in Fig. 2. This apparatus was developed by Sternstein, Ongchin and Silverman and has been described in detail by them (5). For cold drawing, a sample sheet was machined to the shape shown on the left of Fig. 2. The actual sample section dimensions were 4.76 mm wide, 1.52 mm thick and 7 mm long. The shearing was done in an Instron tester by moving the U-shaped jaw while holding the center section

TABLE 1

SAMPLE CHARACTERIZATIONS

Crystallization Temperature	Crystallization Time, Hours	Density gm/cm^3 at 23 C	Density* % Crystallinity	SAX Spacing, Å	SAX Peak** Width (minutes)
127	10	0.975	80.0	530	5.6
125	3	.974	79.4	450	7.2
123	20	.976	80.5	420	8.9
121	20	.975	80.0	390	9.8
127	5	.970	77.3	530	5.6
127	3	.968	76.2	530	5.6
127	1	.963	73.5	530	5.6
Quenched	--	--	68.6	240	18.2

*Based on ideal crystal and amorphous densities of 1.011 gm/cm^3 and 0.852 gm/cm^3 at 23 C.

**Measured at half maximum intensity

stationary. A progression rate of 0.5 cm/min (strain rate of 1.05 min^{-1}) at a temperature of 60C was used throughout. All specimens were deformed to a total nominal strain (total progression divided by gap width) of 4.0 or a "draw-ratio" of 5.0. When the deformation reached this point the sample was unloaded. A typical stress-strain curve for the simple shear deformation is shown in Fig. 3. Table 2 summarizes data on the maximum stress and the stress at maximum strain for each sample.

RESULTS - RETRACTION MEASUREMENTS

Observations to characterize the retraction tendencies of the samples were made in relaxation and creep type testers. The relaxation tester was fitted with jaws similar to those used for the original shearing. Samples which had been strained or cold drawn at 60 C as described above were clamped in this apparatus at room temperature and the jaws constrained against any sample motion. The assembly was then plunged into a silicone oil bath pre-set to the desired test temperature and the stress required to keep the sample from retracting was recorded as a function of time. The creep type tests were similarly performed except that change in sample strain was permitted under constant load or stress.

The results of the relaxation-type tests are summarized in Fig. 4 and 5 showing the retractive stresses developed at temperatures of 70 C and 100 C respectively. The retraction, under zero load, measured in the creep tests is likewise summarized in Figs. 6 and 7.

For the set of samples crystallized at different temperatures the essential difference in structure is the lamellar thickness, or the amount of lamellar fold

TABLE 2

STRESSES RECORDED IN SIMPLE SHEAR DEFORMATION OF POLYETHYLENE SAMPLES

Crystallization Conditions Hours/Temperature	Maximum Observed Stress, Dynes/cm^2	Stress at Maximum Strain, Dynes/cm^2
10/127 C	13.9×10^7	9.40×10^7
3/125	12.9	9.96
20/123	12.9	9.68
20/121	13.0	9.59
5/127	13.0	9.26
3/127	12.2	8.83
1/127	10.9	8.18

surface. If, as has been hypothesized (1, 2) the deformation expands these surfaces or increases the total free energy associated with them, then the samples with the smaller lamellar spacings having the larger amount of surface per unit volume should have the greater tendency to retract. The data summarized at the top of Figs. 4, 5, 6 and 7 would appear to support this hypothesis. In all cases the samples with the smaller lamellar spacings developed the larger retractive stresses or retracted more rapidly. Estimating that the surface or interface area in each sample is inversely proportional to the lamellar thickness or to the SAX spacing, the above hypothesis predicts that the retractive force should be inversely proportional to the SAX spacing. The figures in Table 3 are in reasonable agreement with this considering the uncertainties in making a direct relationship between SAX spacing and crystal surface per unit volume.

The data recorded at the bottoms of Figs. 4, 5, 6 and 7 compare specimens which were all crystallized at the same temperature (127 C) but for different lengths of time so that the densities or "crystallinities" are different. If the amount of crystal surface per unit volume increases with the crystallinity then, again following the above hypothesis, the higher density samples should show the greater tendency to retract. The data, however, indicate just the opposite.

These simple comparisons are, of course, vulnerable to the presence of other differences between samples than the lamellar thickness and "crystallinity" that are being cited as the pertinent parameters between experiments. The influence of varying crystallization temperature and time on other morphological parameters such as interlamellar links and networks is difficult to assess and could markedly influence the course of the deformation and testing. Light microscopy, replica

TABLE 3

COMPARISON OF RETRACTIVE FORCES AND SAX SPACINGS

Crystallization Conditions Hours/Temperature	SAX Spacing Angstroms	Retractive Stress Dynes/cm^2 x 10^{-6}	Stress Multiplied by SAX Spacing
10/127 C	530	9.3 at 70 C	4920
3/125 C	450	11.0 " " "	4950
20/121 C	390	11.5 " " "	4480
10/127 C	530	11.1 at 100 C	5880
3/125 C	450	11.7 " "	5270
20/121 C	390	12.2 " "	4770

electron microscopy and scanning electron microscopy observations were made and revealed no differences among the samples except for the one prepared by quenching the mold from the melt temperature. Sections of the quenched sample when viewed between crossed polars showed ringed spherulites 30μ in diameter with a 2μ ring spacing. The other samples were also composed of 30μ spherulites but no rings were evident. More directly important is the state of the specimens after cold drawing as that is the state in which the retraction characterizations were made and compared.

The simple shear cold drawing was carried to a maximum strain of 4.0 and upon removal of the drawing stress the specimens retracted to a strain of 3.4. They were then cooled to room temperature and no measurable change in strain occurred while specimens were held at room temperature. Characterizations of the orientation in this drawn state were made by wide and small angle Xray scattering. The procedures and results are discussed in a following section. The Xray characterizations confirmed that the set of samples crystallized at different temperatures to the same final density achieved the same state of orientation. This tends to confirm that the differences in retraction behavior in these samples is, as hypothesized, due to the differences in lamellar thickness.

The set of samples all crystallized at 127 C for different times to different final densities did not, however, achieve the same orientation on drawing. Lower density samples became more highly oriented than higher density samples. To ascertain the effect of orientation differences on the retraction behavior, one sample of material which had been crystallized at 127 C for 10 hours was sheared to a maximum strain of 4.5 where it achieved the same state of orientation as a sample crystallized at 127 C for 1 hour and sheared to a maximum strain of 4.0 (More detail of this comparison is given in a following section on the Xray characterizations.) A free

retraction experiment on this specimen showed it to retract more rapidly than the lower density specimen (Fig. 8). This is in agreement with our hypothesis and contrary to the apparent implications of the data at the bottoms of Figs. 4, 5, 6 and 7, which are due to the difference in state of orientation of the specimens. Also consistent with this are the facts that the quenched sample became more highly oriented than any of the others during drawing and exhibited the most rapid free retraction.

Thus, it appears that all of the data recorded on retractive forces and free retraction are consistent with the hypothesis. Still, some discussion of the retraction process itself is called for. In all of the free retraction experiments a rapid initial retraction occurred for the first few minutes followed by a slower continuing retraction which appears linear in relation to the logarithm of time. Similar behavior has been recorded for free retraction of tensile drawn polyethylene and polypropylene (2). In the retractive force measurements (relaxation type tests) at 70 C the force is observed to build up rapidly during the first few minutes and then approaches a value that appears stable. At 100 C, however, a maximum is observed in the retractive force at about 8 minutes followed by a decay or stress relaxation.

Following the conclusions of Steiñ (6, 7) based on his extensive characterization of the deformation of spherulitic polyethylene, this retraction behavior may be interpreted as follows: During the initial drawing two primary deformations occur; an interlamellar and/or interspherulitic mode and an intralamellar process. The first, which accounts for only a very small fraction of the total strain is rapidly and essentially completely recovered when the drawing load is removed. A part of the

intralamellar deformation is also recovered, that corresponding to the rapid retraction which would occur at 60 C, the drawing temperature. The measurement of retractive forces show a development of the retractive force during the first few minutes which is related to a retraction of the interlamellar deformation coupled to re-deformation or tightening of the intralamellar network. The longer-time decay of the retractive force at 100 C is attributed to interlamellar creep, leaving the question as to how near the potential retractive force is the observed maximum?

The data recorded in Fig. 9 show the results of relaxation tests on four oriented samples at 23, 50, 60 and 70 C, pre-loaded to a stress of 14.8×10^6 dynes/cm^2 at 23 C. This pre-loading should have oriented the interlamellar network. At 23 C only a relatively slow decay of the stress is observed. At 50 C and 60 C a rapid initial relaxation is observed which may be related to intralamellar orientation coupled with interlamellar disorientation until the stresses to balance the two modes is achieved. At 70 C further rapid intralamellar retraction is activated and so, following an initial stress decay, the stress is seen to rise and then stabilize. Because the specimens were originally drawn at 60 C, and because after removal of the drawing load both interlamellar an intralamellar retraction occurs, there is little or no driving force for intralamellar retraction activated in the tests at or below 60 C. While an apparently stable stress appeared to develop for the three higher temperature tests, the 23 C test did not stabilize probably due to much slower response at this lower temperature.

Figure 10 presents the results of a relaxation type test in which the stress was permitted to reach a stable value at 70 C before the temperature was decreased to

60 C for 60 minutes and then returned to 70 C. The stress followed this by decreasing when the temperature was lowered and returning to the same value when the temperature was returned to 70 C. A contrast is offered by the relaxation data obtained for a similar loading on undrawn specimens. As is seen in Fig. 11, the stress quickly decays to values much smaller than for the oriented specimens and continues to decay with time. The decay is more rapid at 100 C than at 70 C. From the shape of the original cold drawing curves it is estimated that at the stresses encountered in these tests, the induced interlamellar deformation accounts for no more than three percent strain. Comparing this to the difference between samples drawn to different extents leads to an estimate that the partial relaxation of the intralamellar orientation to affect the interlamellar network tightening in the retractive force measurement tests would cause only a few percent decrease in the measured potential retractive force. It is, therefore, concluded that the stable stress values recorded in the 70 C tests are a true measure of the potential retractive force within a few percent. The evident relaxation occurring within the experimental time scale leaves a larger uncertainty in the potentially achievable retractive force at 100 C. However, comparison of the data at 100 C to those at 70 C and of the temperature cycled force measurement (Fig. 10) establishes the positive sign of the temperature coefficient of the force. The hypothesis that the retractive force is related to crystal surface or interface free energy is not inconsistent with this. The deformation changes both the interface area and the character of the interface. The fold surface, for example, becomes larger but its orientation with respect to the unit cell changes. We may interpret the positive temperature coefficient as indicating that deformed interface has a lower entropy than the undeformed interface.

CHARACTERIZATION OF ORIENTED STRUCTURE

Most of the research on cold-drawing of crystalline polymers has used a tensile extension to deform and orient the sample. As noted previously, Stein (6, 7) has shown that the mechanical response can be interpreted in terms of an essentially elastic interlamellar/interspherulitic deformation with a very rapid response in series with a slower intralamellar deformation. Probably the most extensive studies of the structural character of the deformation have been made by Peterlin and his colleagues. A recent paper presents specific results on cold drawing of high density polyethylene (8). Peterlin's interpretation has the drawing process begin with lamellar rotation and reorientation (interlamellar deformation) followed by slip and tilting of molecules within lamellae (intralamellar deformation) and eventually breaking of lamellae to form new fibrils. Work in this laboratory (9) on tensile drawing of rods of high density polyethylene (similar to that used in this study) is in agreement with Peterlin's model but suggests that while the lamellae deform relatively little breaking up occurs until the draw ratio exceeds 4 or 5.

The simple shear deformation differs from tensile drawing in two primary features of concern here. One, the symmetry of the orientation which results is different. Two, the dilatational stress influences may be different in that a tensile drawn sample is more free to expand (decrease in density) than is a simple shear specimen. An affine, constant volume, tensile deformation of a sphere produces an ellipsoid with circular symmetry about the extension axis. An ideal, constant volume simple shear deformation of a sphere proceeds as indicated in Fig. 12. The plane of maximum strain starts out at 45^{o} to the plane of the applied shear stress and rotates with increasing strain toward a direction parallel to the plane of the applied

shear stress. In the plane of maximum strain, which expands in area, the circular section of a sphere grows in one direction while remaining of constant width in the other. The simple shear to strains of 4 as performed in this study are not expected to follow this ideal any more than a tensile drawing is expected to be affine and constant volume. However, examination of several specimens with wide and small angle Xrays from many directions consistently confirmed that the primary orientation direction was essentially coincident with the ideal plane of maximum deformation and the symmetry was as would be expected from this idealized picture.

Figure 13 presents two typical wide angle Xray patterns taken on a specimen crystallized for 10 hours at 127 C before and after cold-drawing. The Xray diffraction was done on a General Electric XRD-3 unit with a copper target. Further details of this apparatus and procedure have been described by Muzzy (4) and by Falender (10). Densitometer traces about the (200) and (110) rings indicate orientation of the drawn specimen in the direction expected based on the idealized picture of the simple shear deformation as may be seen from Fig. 14. There is some evidence of a second shoulder distorting the peak on the (200) ring trace. In the simple shear deformation the dilatational stress which develops is countered by a stress normal to the shear stress which arises because the sample is constrained in that direction (5). Applying modest tensile stress in this direction tended to decrease the shoulder suggesting that this stress may be the cause of the shoulder.

Unit cell or molecular orientation characterizations were made by measuring the widths of the (200) intensity traces at one half maximum intensity. These results, and some similar (110) characterizations are recorded in Table 4. Essentially

identical half widths were obtained for the samples which had been crystallized at different temperatures to the same final densities. However, for the series crystallized at 127 C for different times the half widths range from 59 to 74 degrees indicating greater orientation for the lower density samples. When the maximum shear on the 10 hour/ 127 C sample was increased from 4.0 to 4.5 the half width decreased from 81 to 72 degrees making it more comparable to the lower density samples. The quenched sample achieved the greatest orientation.

In Table 5 some wide angle orientation characterizations are recorded for specimens after free retraction and retractive force tests. When a sample is constrained and heated to 70 C in a retractive force test the width decreases from 81 degrees to 68 degrees indicating an improvement in orientation associated with the tightening or re-orientation of the interlamellar network. In a similar test at 100 C the widths after 700 minutes are as before the test. Presumably the re-orientation of the interlamellar network has been compensated by disorientation related to intralamellar relaxation which is reflected in the observed decay of the retractive force.

In the free retraction tests an improvement in orientation is also noted after 2 minutes at 100 C, but after 2000 minutes the orientation has decreased below that prior to the retraction. Again, during the initial period of rapid retraction the interlamellar network may re-orient more than compensating, temporarily, for the decreasing orientation associated with intralamellar retraction. In the longer run however, this orientation is lost. At 70 C, where the total retraction is less, there is evidence only of a small decrease in orientation. A comparison may also be made of the relative effects of free retraction at 100 C of samples originally crystallized 10 hours/127 C, 1 hour/127 C and 20 hours/121 C. The sample crystal-

TABLE 4

WIDE ANGLE XRAY DIFFRACTION

WIDTH OF 200 PEAK AT HALF MAXIMUM INTENSITY

IN SHEARED SPECIMENS

Sample Crystallization Hours/Temperature	Width of (200) Peak Degrees
10/127	81
3/125	81
20/123	81
20/121	78
5/127	74
3/127	74
1/127	59
Quenched	49
10/127*	72

*This specimen sheared to maximum strain of 4.5, all others sheared to maximum strain of 4.0.

TABLE 5

WIDE ANGLE XRAY DIFFRACTION ORIENTATION CHARACTERIZATION AFTER RETRACTION TESTS

TEST	Width at 1/2 Maximum Intensity Degrees (200)	(110)
None	81	103
Retractive Force Test, 2000 min. at 70C	68	93
700 min. at 100C	81	103
Free Retraction, 2000 min.at 70C	81	106
2000 min. at 100C	87	109
2 min. at 100C	62	
Free Retraction, 2000 min. at 100C*	81	
2000 min. at 100C**	87	

Samples were crystallized at 127 C for ten hours and sheared to a maximum strain of 4.0 at 60 C prior to mechanical tests except as marked by asterisks.

*This sample crystallized at 127 C for 1 hour

**This sample crystallized at 121 C for 20 hours

lized at 1 hour/127 C is of lower density, orients the most during cold drawing, retracts the most and shows the largest decrease in orientation, the (200) width increasing from 59 degrees to 81 degrees after 200 minutes free retraction at 100 C. The sample crystallized 20 hours/121 C has the same original density as the one crystallized 10 hours/127 C, appears slightly more oriented after drawing but disorients equivalently more during free retraction corresponding to the observed greater retraction.

Some small angle Xray scattering patterns were also obtained using the GE XRD-3 unit with a copper target and a Statton-Warhus type camera. Details of the apparatus and procedure have been described by Falender (10). Figure 15 presents two typical SAXS patterns obtained on sheared specimens. Again, these patterns are similar to patterns obtained from tensile drawn materials if the direction of maximum strain is compared to the draw axis in tension. One difference is some evidence of scattering along the vertical direction which is presumed due to the normal stress effect described above in reference to the wide angle pattern. Densitometer traces of the SAXS patterns were taken about an arbitrarily chosen circle corresponding to spacing of 175 Å. The width of the "equatorial" scattering peaks at one half maximum intensity were used in characterizing the relative lamellar orientations for a selected set of samples as recorded in Table 6. (The "equatorial" scattering is most probably due to oriented voids and dilations but the prior work of Muzzy (4) suggests that these form at lamellar boundaries and their orientation corresponds to the lamellar orientation). Both the sample crystallized 10 hrs./127 C and the one crystallized 20 hrs./ 121 C have the same 43 degree SAXS width after drawing, again confirming that the samples of similar density with different lamellar thicknesses achieved the same state of orientation after drawing. The lower density sample, crystallized 1 hour/127 C has a 68 degree width indicating lesser lamellar orientation. As the wide angle results

TABLE 6

SMALL ANGLE XRAY SCATTERING

Width of "Equatorial" Scattering Peak Measured at Half Maximum Intensity of Trace on Circle Corresponding to 175 Angstrom Spacing

Sample	Half Width, degrees
Crystallized 10 hrs./ 127 C, drawn	43
Crystallized 20 hrs./ 121 C, drawn	43
Crystallized 1 hr./ 127 C, drawn	68
Crystallized 10 hrs./ 127 C, drawn	
plus free retraction 2000 minutes at 70C	71
plus free retraction 2000 minutes at 100C	77
plus free retraction 2 minutes at 100C	74
plus relaxation test 2000 minutes at 70C	71
plus relaxation test 700 minutes at 100C	83
Crystallized 20 hrs./121 C, drawn	
plus free retraction 2000 minutes at 100C	93
Crystallized 1 hr./127 C, drawn	
plus free retraction 2000 minutes at 100C	93

indicated greater orientation on drawing for the lower density samples it appears that this occurs by intralamellar deformation coupled to lesser lamellar orientation The interpretation of the overall deformation as an interspherulitic/interlamellar mode coupled in series with an intralamellar mode is, of course, an oversimplification as to some degree there must also be a parallel coupling of the two modes. In both free retraction tests and retractive force (relaxation) tests lamellar disorientation is observed with the magnitude being larger at 100C than at 70C. In these, and the wide angle, characterizations of the specimens used for retractive force measurements the samples were cooled to room temperature and then removed from the jaws. It is possible that some further dis-orientation of these stressed samples occurred on unloading.

All of the samples used in this study, except for the "quenched" one had been crystallized relatively slowly at comparatively high temperatures. The significance of this may be seen in the density data recorded in Table 7. All samples decreased in density on drawing and increased in density (to near the original values) after creep or relaxation tests. The quenched sample, however, increased in density to a value higher than its original value. That an annealing or re-crystallization of this sample occurred was confirmed by annealing an undrawn, quenched sample at 100C and observing the same density increase.

CONCLUSIONS

The association of a retraction tendency or long range entropy elasticity with the surface free energy of deformed, oriented lamellar polyethylene crystals is confirmed by the results of this study. The deformation of a crystalline or semi-

TABLE 7

DENSITY CHARACTERIZATIONS

gms/cm^3 at 23C by density gradient column

Crystallization hours/temperature	10/127C	20/121C	1/127C	Quenched
Before Drawing	.975	.975	.963	.955
Drawn	.962	.967	.959	.956
Drawn plus free retraction at 100 C	.974	.975	.968	.966
Drawn plus relaxation test at 100 C	.972	.974	.967	--
Annealed undrawn at 100 C	.975	.975	.963	.967

crystalline polymer is a complex process of coupled deformations in different phases at several structural levels and is not yet completely understood. Undoubtedly there may be elastic effects associated with several modes. In materials with a significant amorphous fraction rubberlike elasticity associated with molecular orientation in the amorphous fraction should be expected. The specimens used in this study were deliberately chosen and prepared to emphasize effects associated with crystal phase deformation. The morphological parameters, lamellar thickness and density, were deliberately varied and the effects on the elastic response were consistent with the hypothesis.

ACKNOWLEDGMENTS

This research was supported by the U.S. Army Research Office-Durham, North Carolina. The experimental work was performed at Rensselaer Polytechnic Institute's Materials Research Center supported in part by the National Aeronautics and Space Administration.

This research was a part of the doctoral dissertation of James R. Falender.

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FIGURE CAPTIONS

FIGURE 1. SMALL ANGLE XRAY DIFFRACTION AFTER SUBTRACTION OF DIFFUSE SCATTER

FIGURE 2. DIAGRAM OF SAMPLE SHAPE AND SIMPLE SHEAR JAWS

FIGURE 3. TYPICAL STRESS-STRAIN CURVE FOR SIMPLE SHEAR OF POLYETHYLENE

FIGURE 4. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 70C

FIGURE 5. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 100C

FIGURE 6. RETRACTION IN CREEP TEST AT ZERO STRESS AT 70C

FIGURE 7. RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C

FIGURE 8. COMPARISON OF RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C FOR SAMPLE SHEARED TO DIFFERENT EXTENTS. BOTH SPECIMENS ORIGINALLY CRYSTALLIZED AT 127C FOR 10 HOURS

FIGURE 9. RELAXATION AT DIFFERENT TEMPERATURES FROM ORIGINAL STRESS OF 14.8×10^6 dynes/cm^2 IMPOSED AT 23C. SAMPLES ORIGINALLY CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C

FIGURE 10. RESPONSE OF RETRACTIVE STRESS IN RELAXATION EXPERIMENT TO CHANGES IN TEMPERATURE. SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C.

FIGURE 11. STRESS RELAXATION IN UNORIENTED SPECIMENS FROM ORIGINAL STRESS OF 14.8×10^6 dynes/cm^2 IMPOSED AT 23C.

FIGURE 12. DEFORMATION OF A SPHERICAL ELEMENT IN IDEALIZED SIMPLE SHEAR

FIGURE 13. XRAY DIFFRACTION PATTERN FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C (LEFT) AND AFTER SHEARING AT 60C TO A STRAIN OF 4.0 (RIGHT).

FIGURE 14. DENSITOMETER TRACE OF (200) RING FROM FIGURE 13 (RIGHT)

FIGURE 15. SMALL ANGLE XRAY SCATTERING DIAGRAM FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED AT 60C TO STRAIN OF 4.0 (LEFT) AND DENSITOMETER TRACE AT 175 Å (RIGHT)

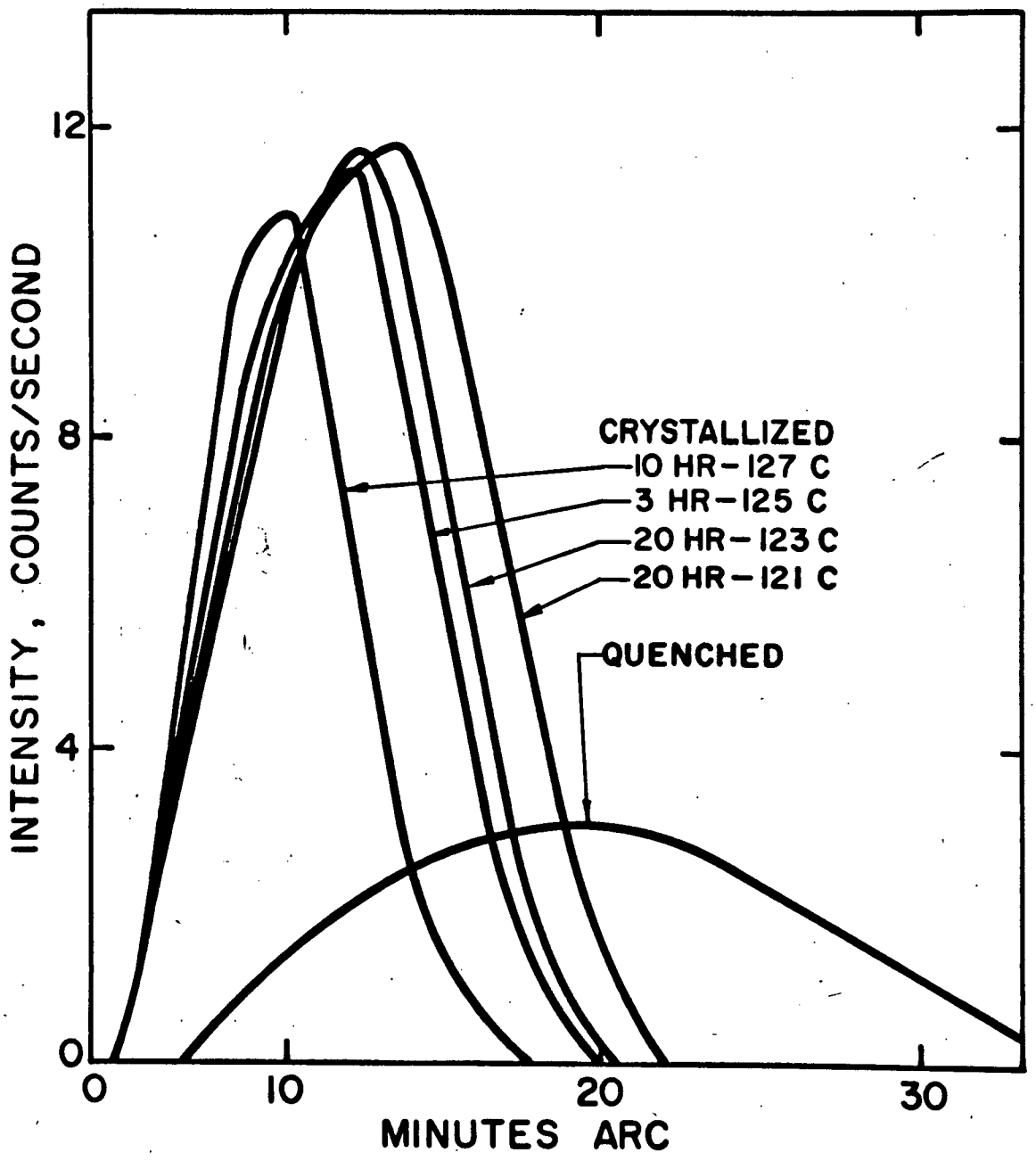
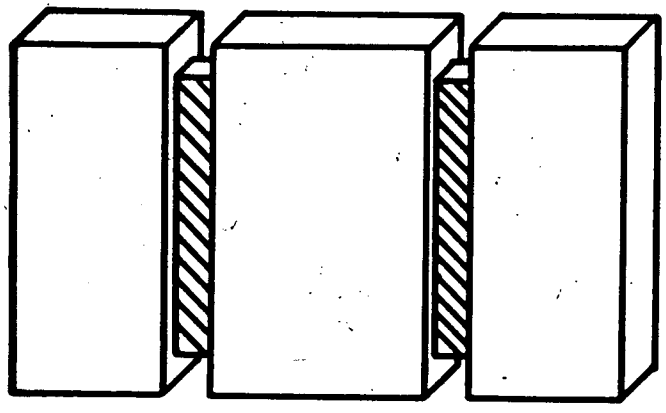
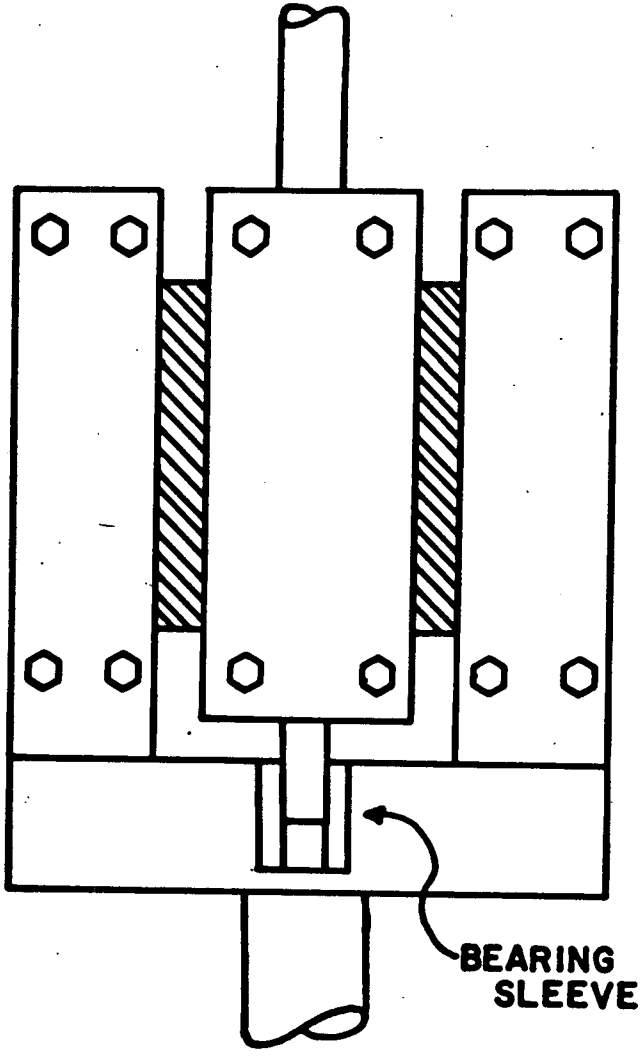


FIGURE 1. SMALL ANGLE XRAY DIFFRACTION AFTER SUBTRACTION OF DIFFUSE SCATTER



SAMPLE



SHEAR JAWS

FIGURE 2. DIAGRAM OF SAMPLE SHAPE AND SIMPLE SHEAR JAWS

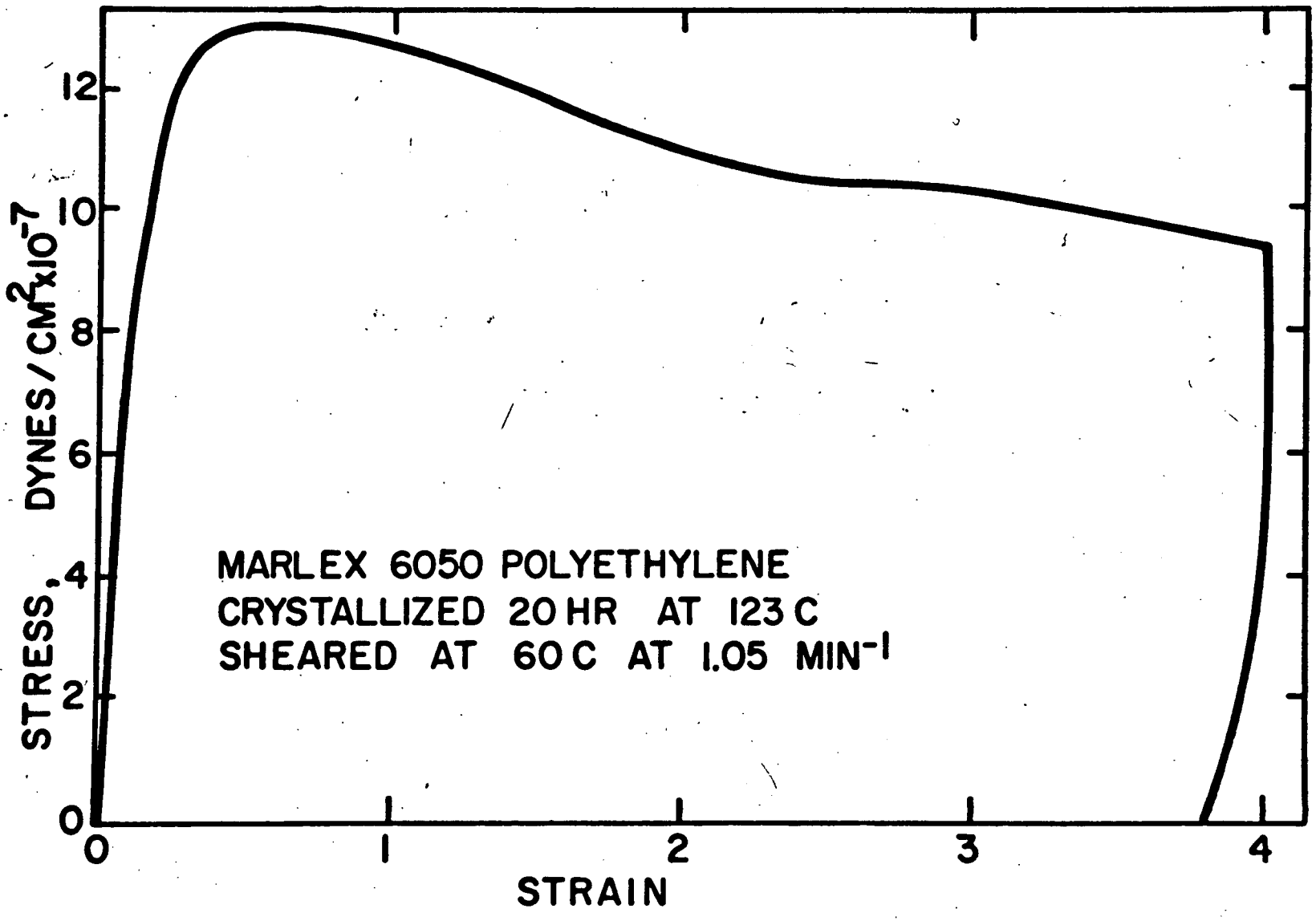
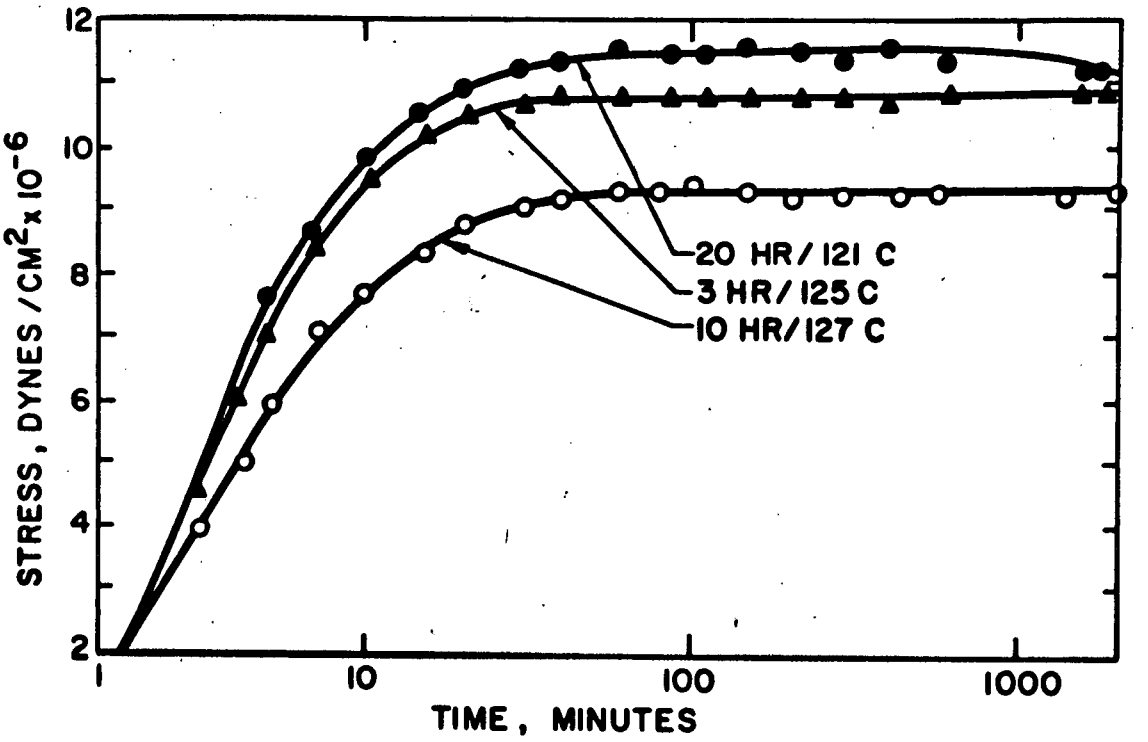


FIGURE 3. TYPICAL STRESS-STRAIN CURVE FOR SIMPLE SHEAR OF POLYETHYLENE



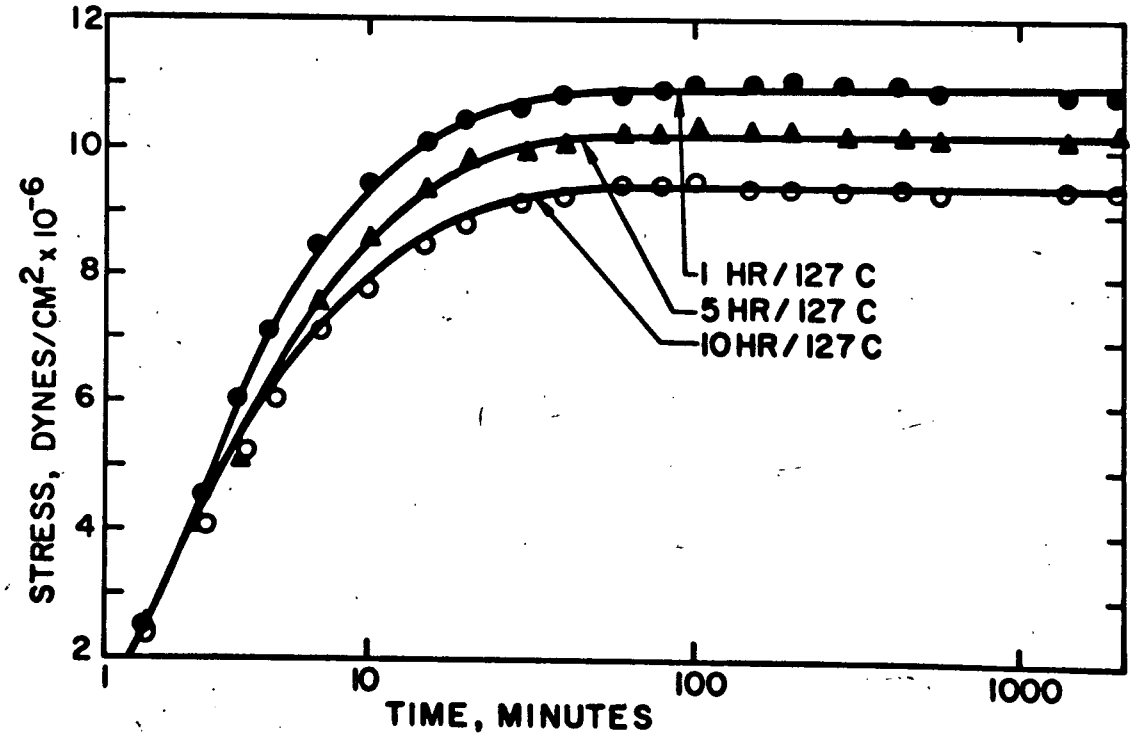
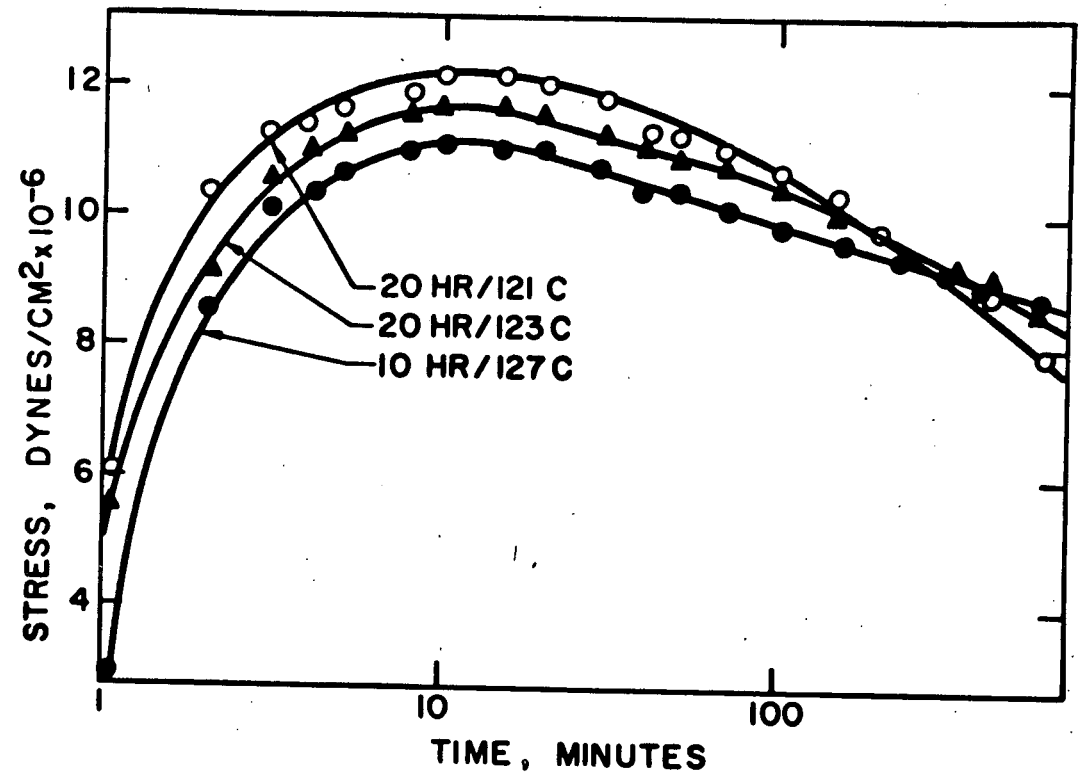


FIGURE 4. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 70C



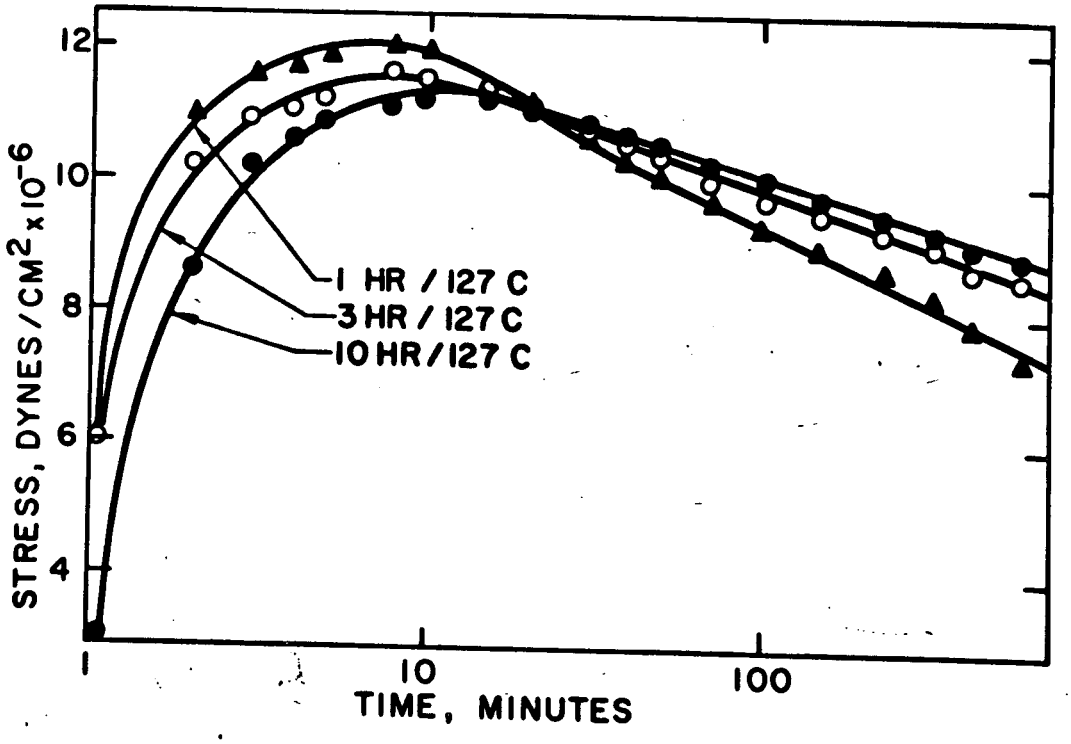
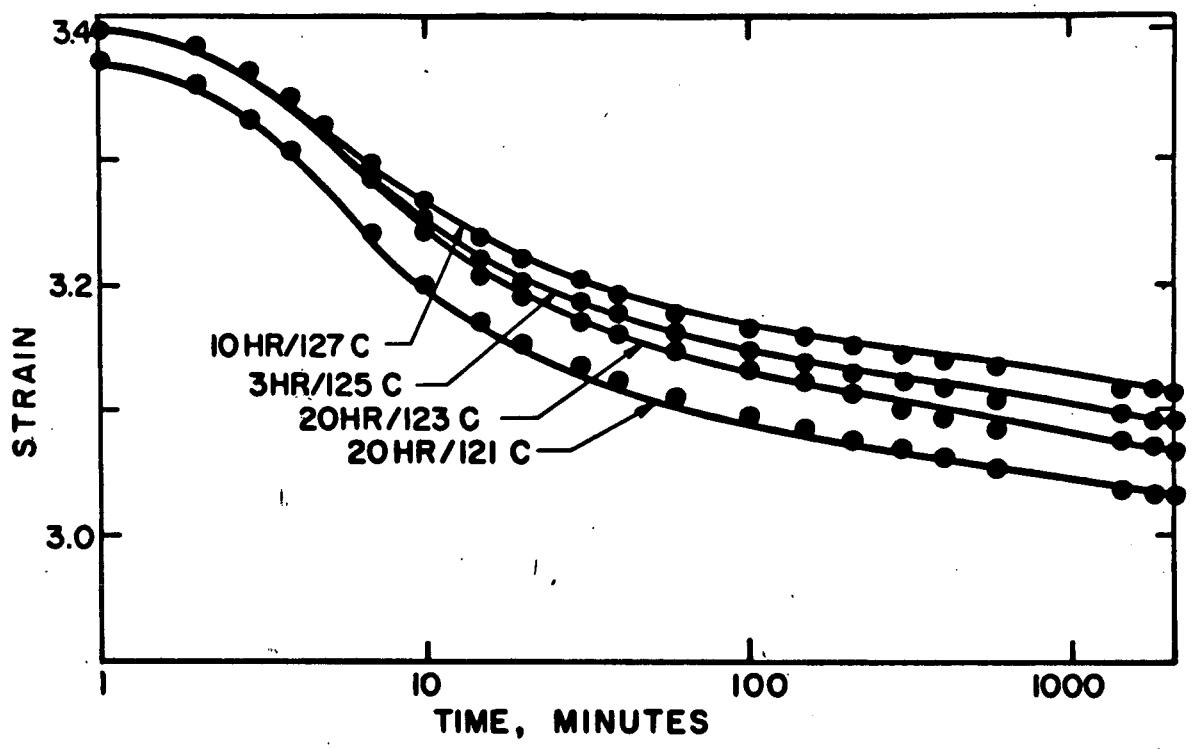


FIGURE 5. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 100C



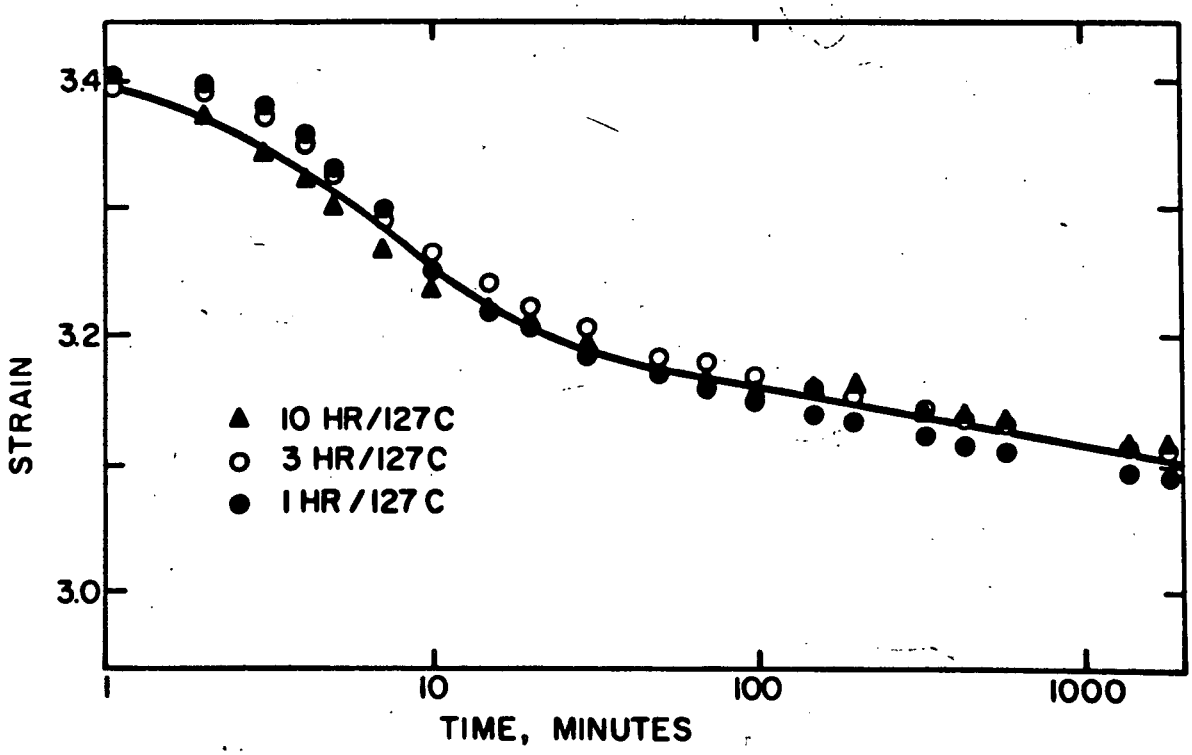
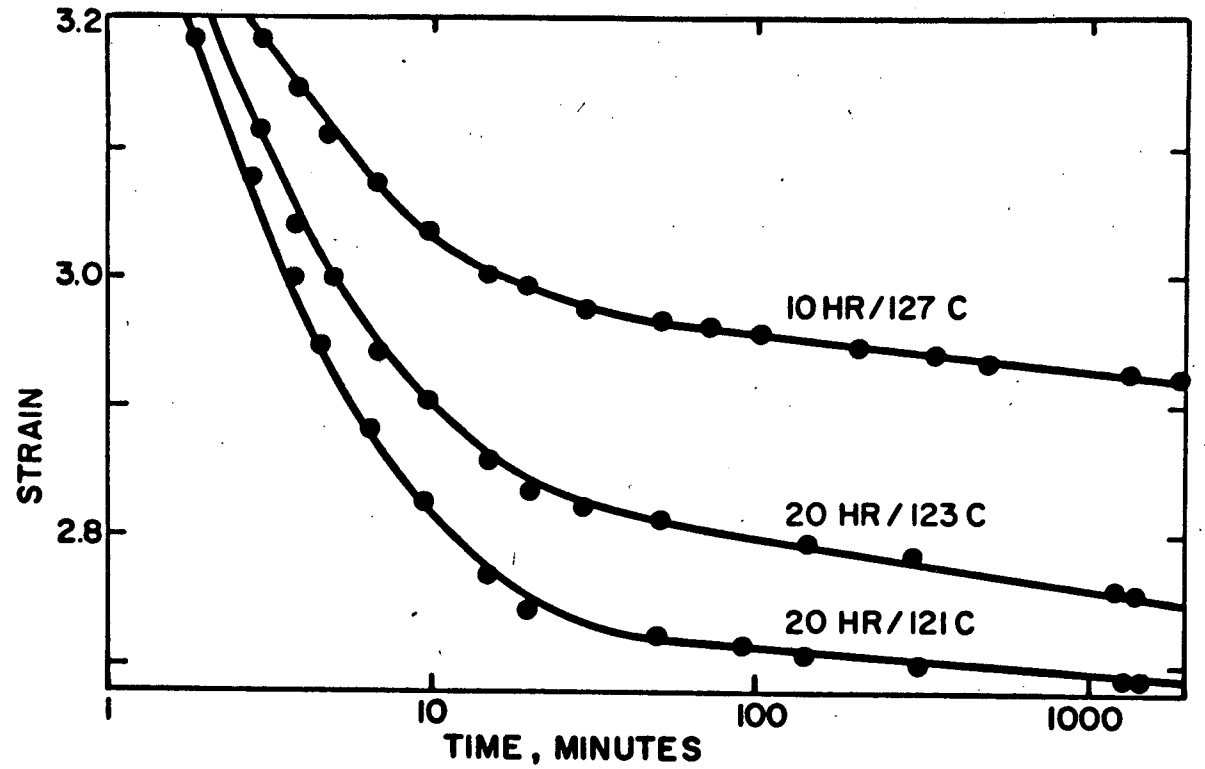


FIGURE 6. RETRACTION IN CREEP TEST AT ZERO STRESS AT 70C



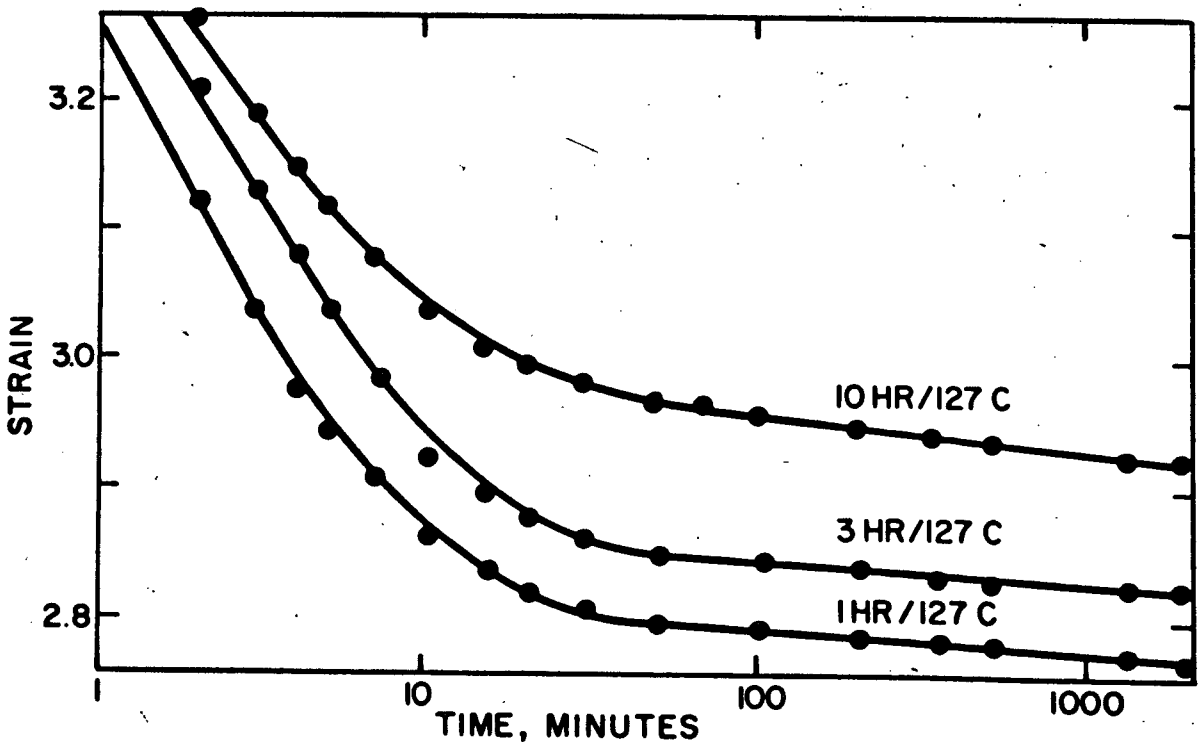


FIGURE 7. RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C

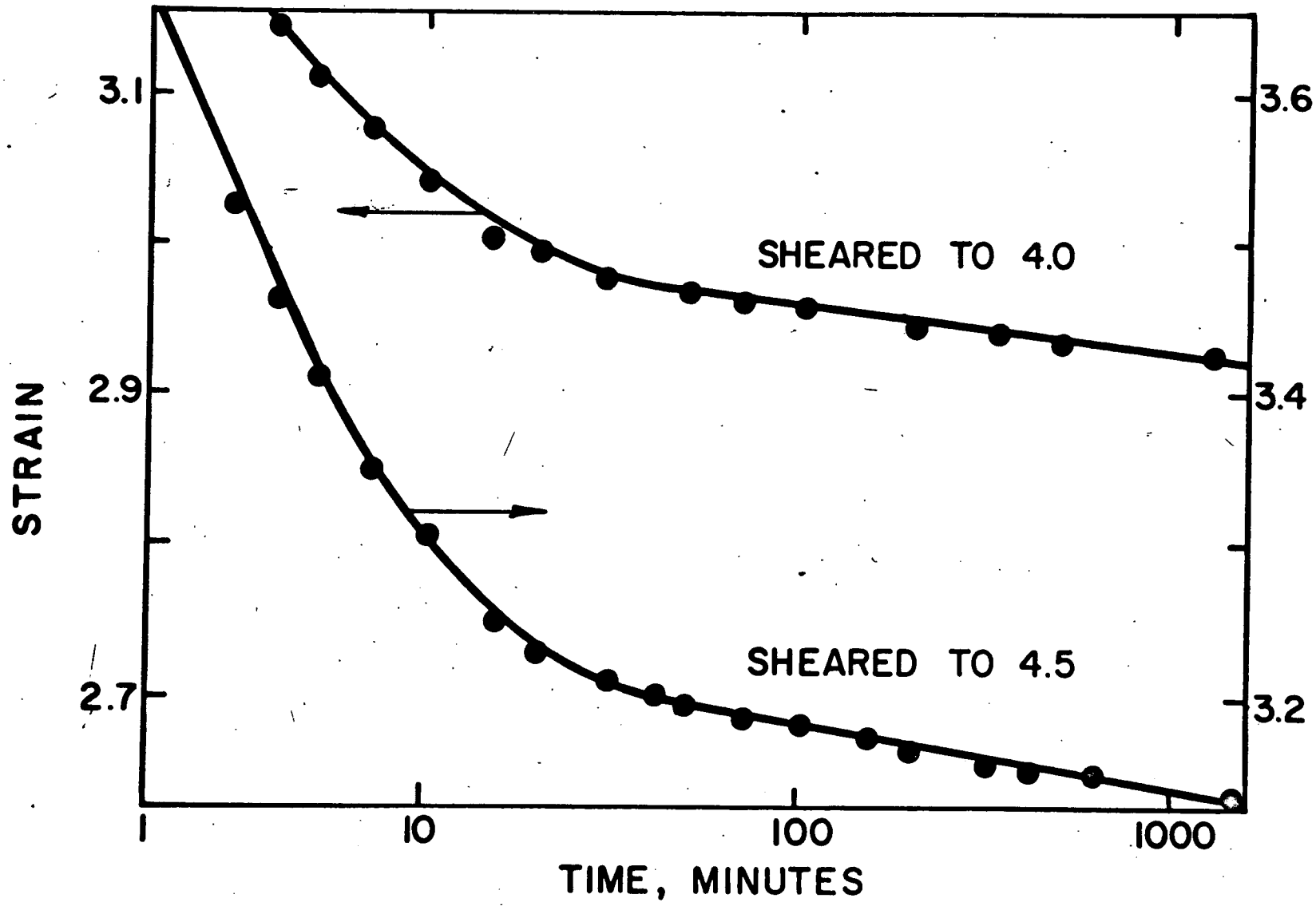


FIGURE 8. COMPARISON OF RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C FOR SAMPLE SHEARED TO DIFFERENT EXTENTS. BOTH SPECIMENS ORIGINALLY CRYSTALLIZED AT 127C FOR 10 HOURS

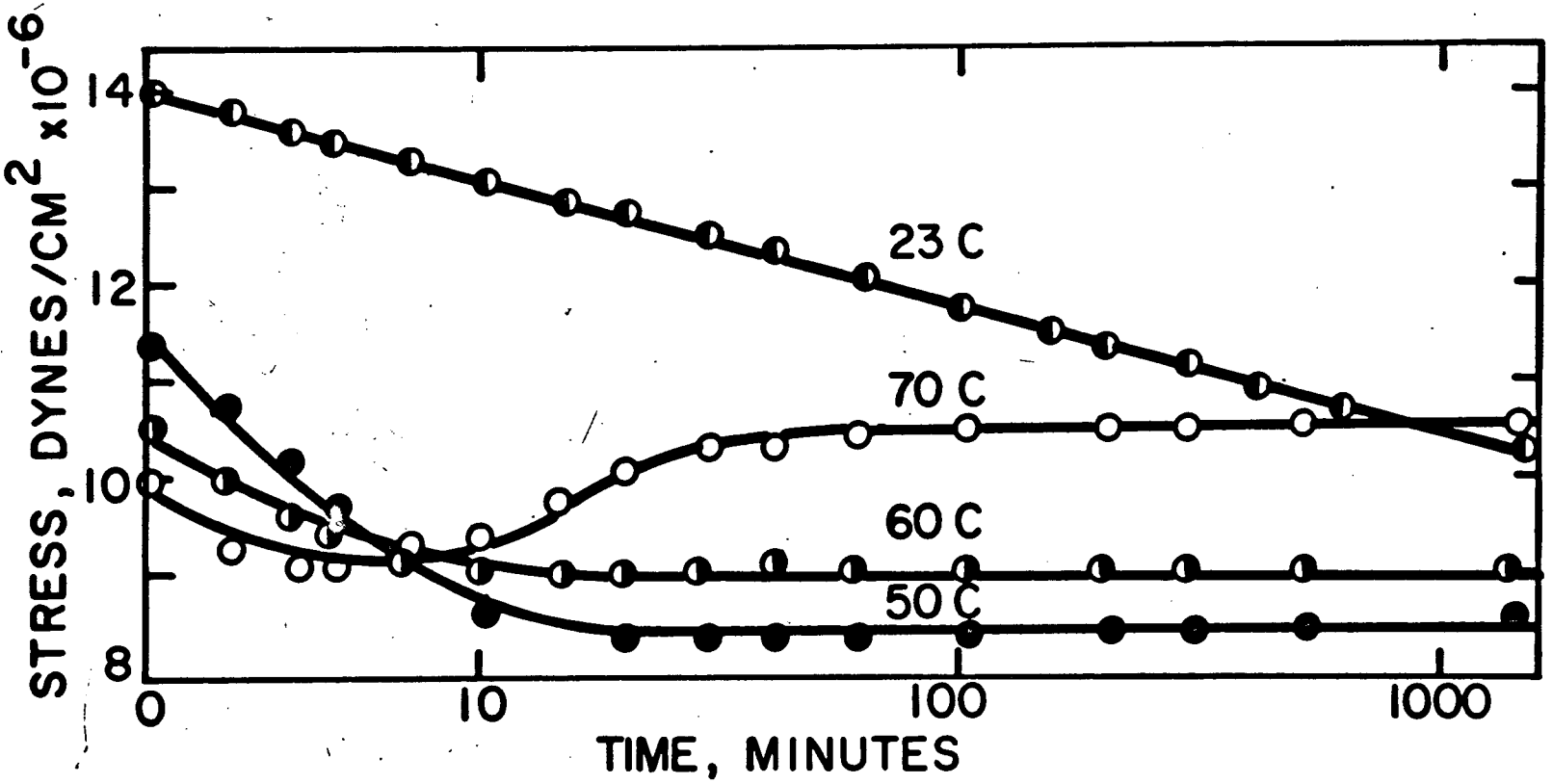


FIGURE 9. RELAXATION AT DIFFERENT TEMPERATURES FROM ORIGINAL STRESS OF 14.8 x 10^6 dynes/cm^2 IMPOSED AT 23C. SAMPLES ORIGINALLY CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C

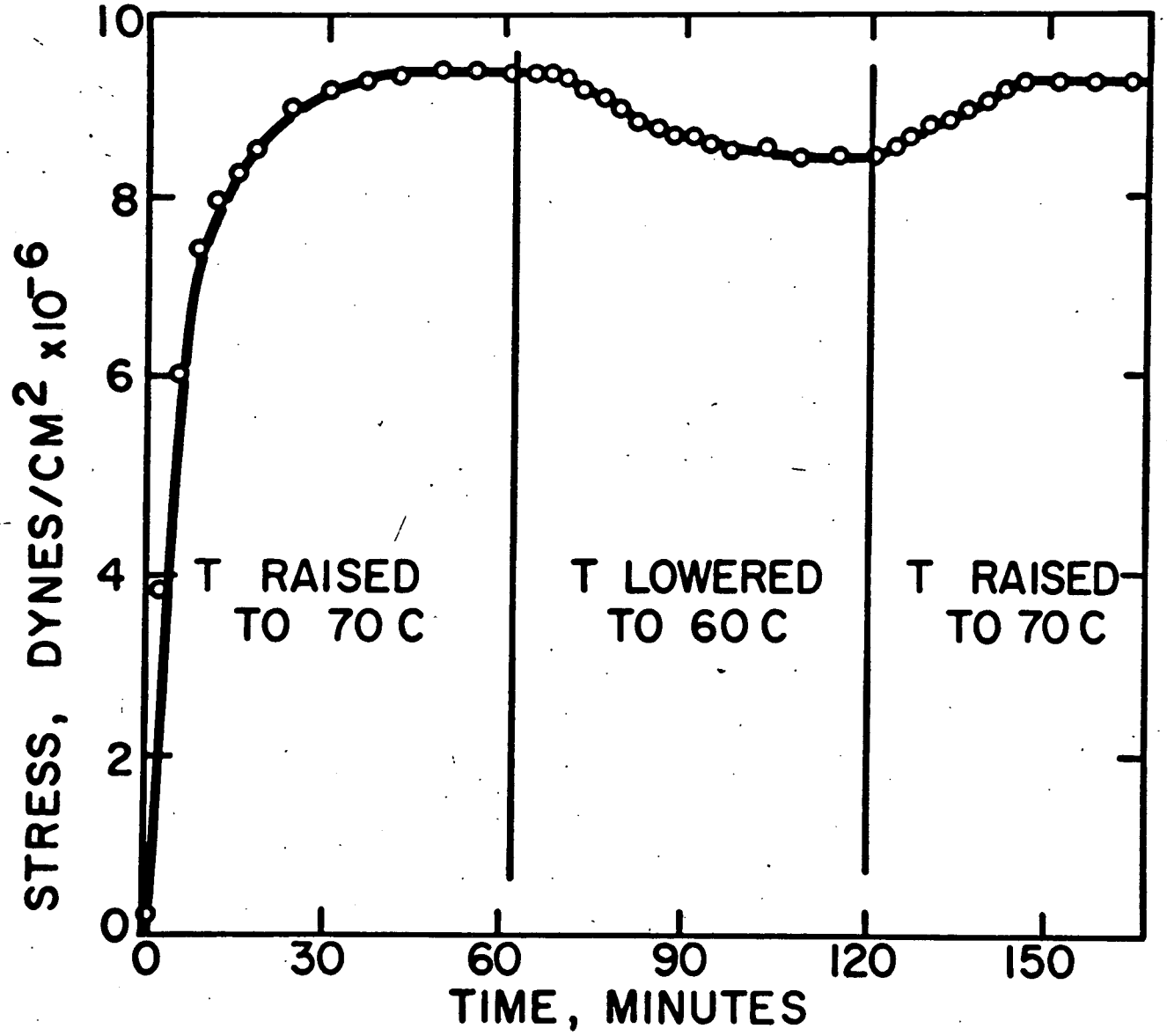


FIGURE 10. RESPONSE OF RETRACTIVE STRESS IN RELAXATION EXPERIMENT TO CHANGES IN TEMPERATURE. SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C.

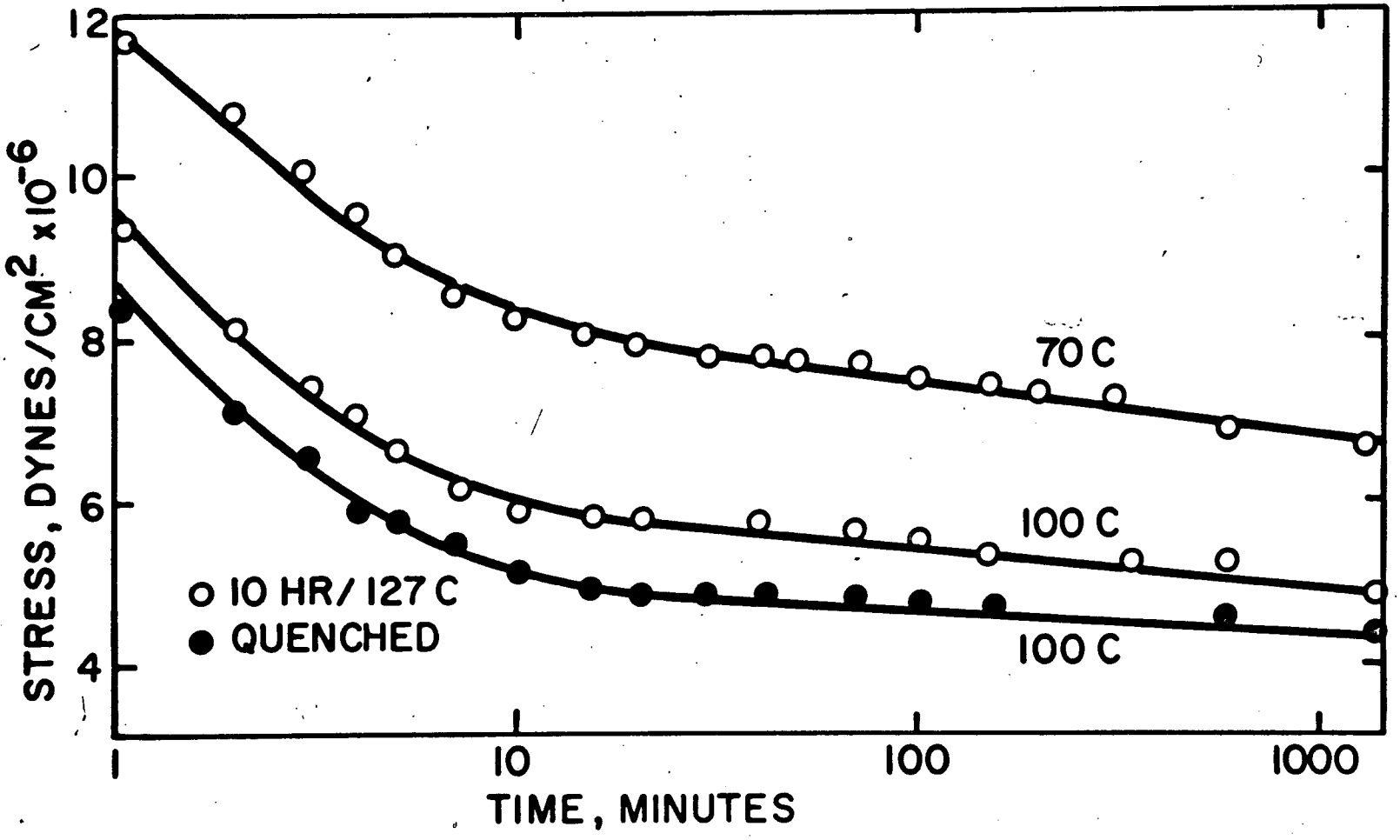


FIGURE 11. STRESS RELAXATION IN UNORIENTED SPECIMENS FROM ORIGINAL STRESS OF 14.8×10^6 dynes/cm^2 IMPOSED AT 23C.

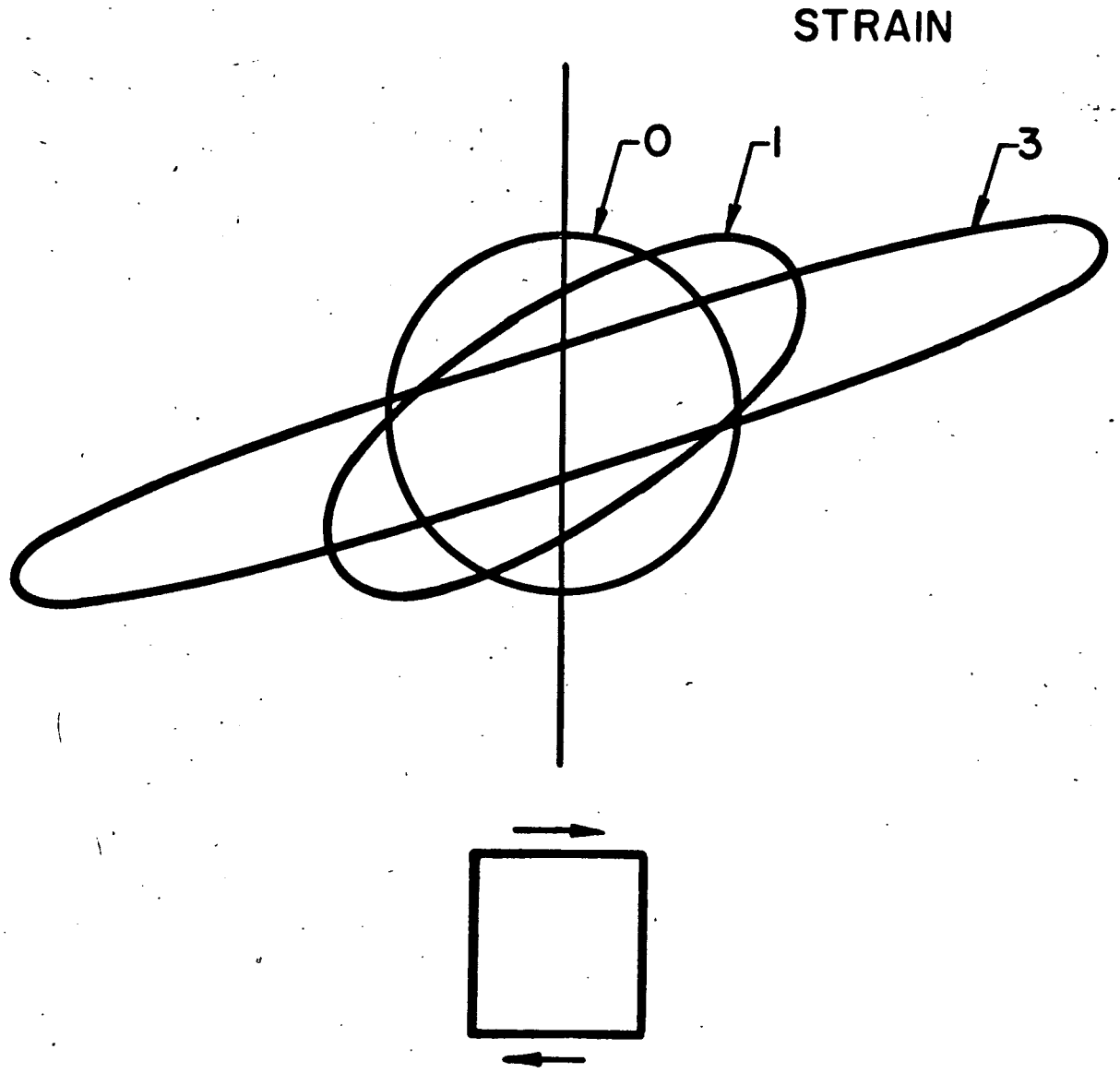


FIGURE 12. DEFORMATION OF A SPHERICAL ELEMENT IN IDEALIZED SIMPLE SHEAR

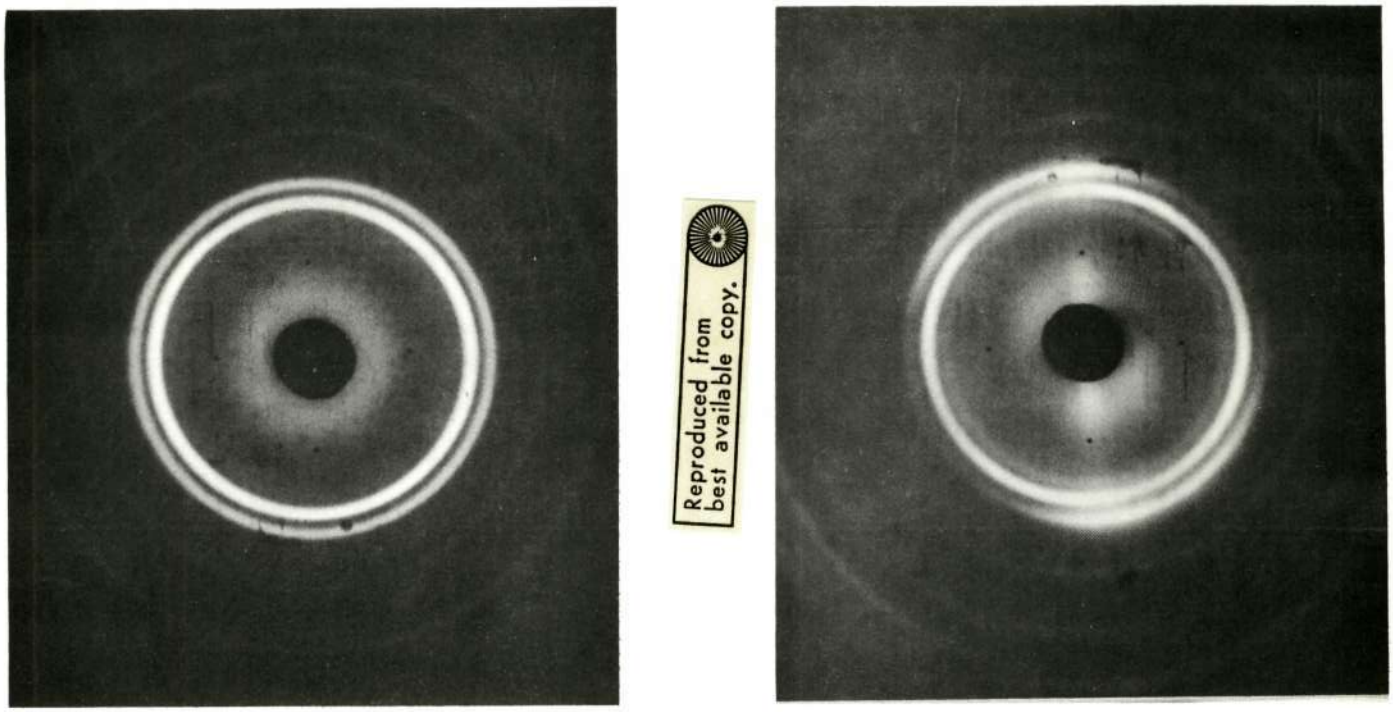


FIGURE 13. XRAY DIFFRACTION PATTERN FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C (LEFT) AND AFTER SHEARING AT 60C TO A STRAIN OF 4.0 (RIGHT)

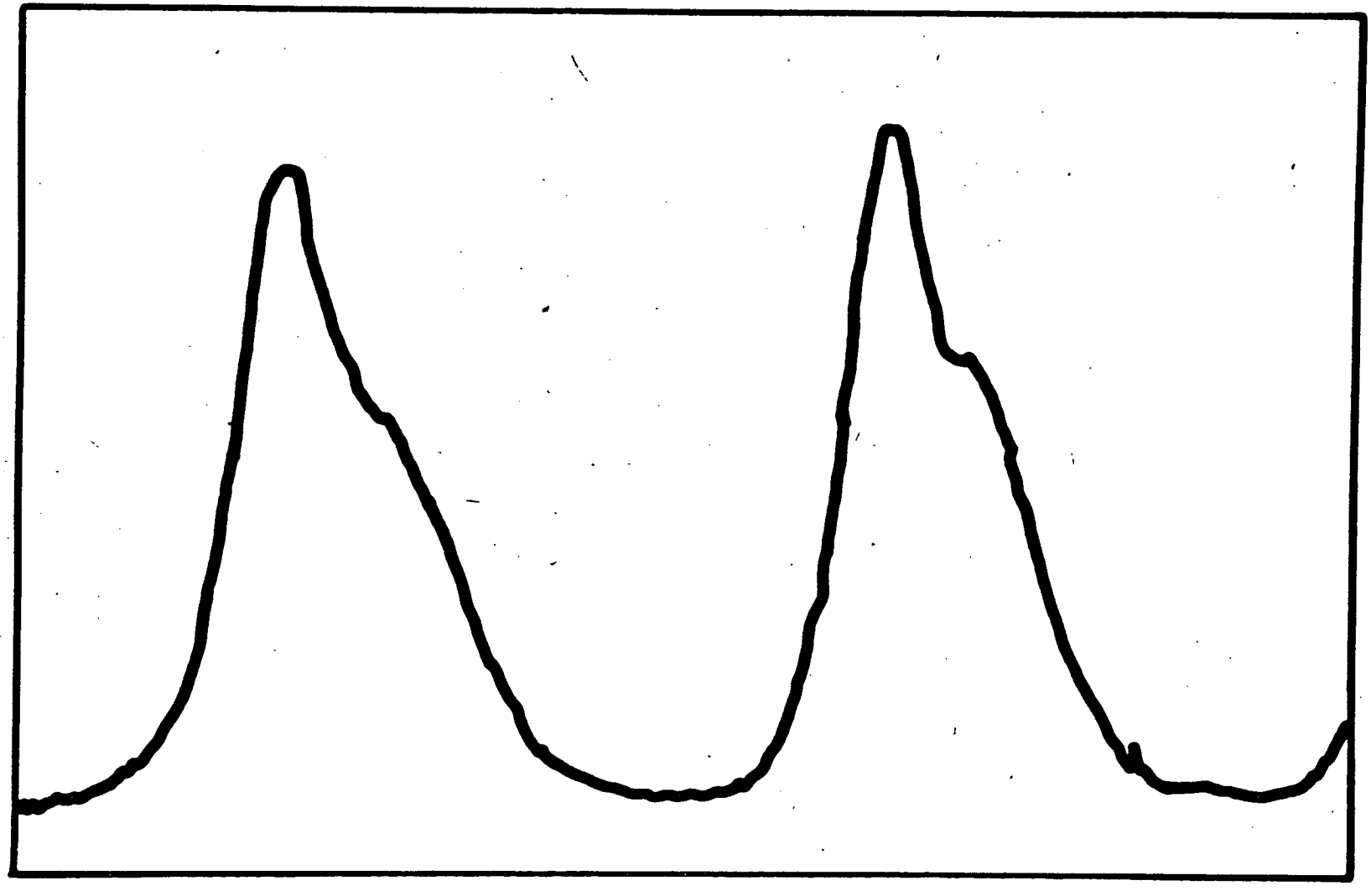
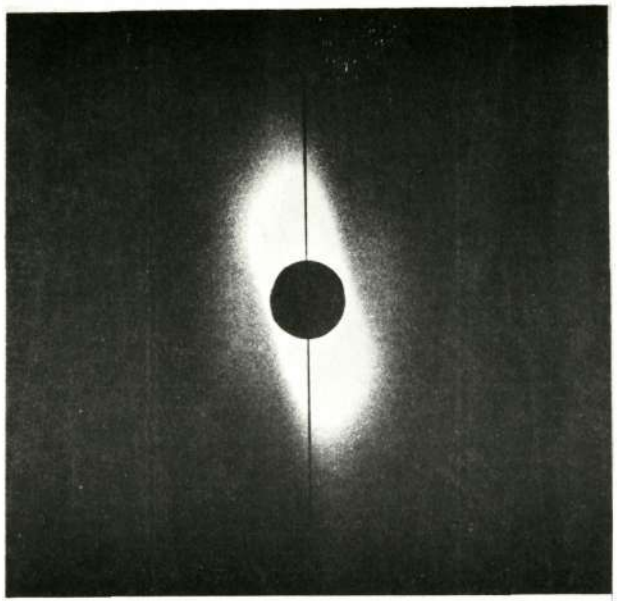


FIGURE 14. DENSITOMETER TRACE OF (200) RING FROM FIGURE 13 (RIGHT)



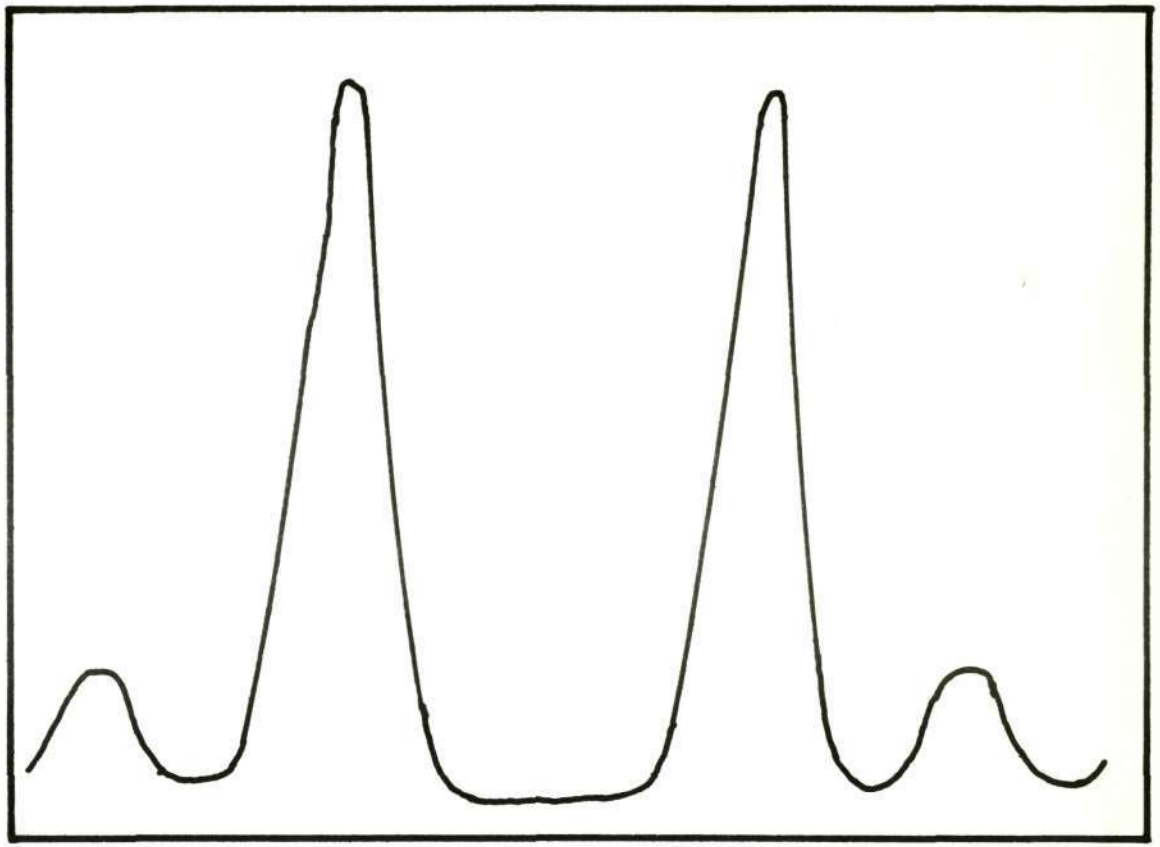


FIGURE 15. SMALL ANGLE XRAY SCATTERING DIAGRAM FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED AT 60C TO STRAIN OF 4.0 (LEFT) AND DENSITOMETER TRACE AT 175 Å (RIGHT)

RETRACTION OF COLD DRAWN POLYETHYLENE: THE INFLUENCE OF LAMELLAR THICKNESS AND DENSITY

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and

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August 1971

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ABSTRACT

The role of crystal morphology in the retraction of oriented, linear polyethylene was studied utilizing samples crystallized under conditions controlled to vary, separately, lamellar crystal thickness and density. Samples were oriented in a simple shear deformation to a strain of 4.0 prior to measuring retraction tendency in creep and relaxation type tests. Characterizations of specimens were made using wide and small angle Xray techniques. The specific morphological variations were chosen to test the hypothesis that a long range elastic restoring force can originate in conjunction with deformation of lamellar crystals and the consequent increase in lamellar crystal surface area and surface free energy. The results support this hypothesis.

INTRODUCTION

When a crystalline linear high polymer is oriented by mechanical deformation, as in cold-drawing, it retains a tendency to retract or to revert to its underformed state. Heating the specimen above the drawing temperature speeds the retraction and also apparently increases the magnitude of the retraction. At temperatures near the melting point of the polymer, nearly complete recovery from deformation can be observed. This behavior has been known for some time and has been widely attributed to "rubber elasticity" associated with orientation of molecules in the amorphous regions of "semi-crystalline" polymers. While this interpretation may be useful in viewing the response of materials of relatively low crystallinity or materials having an identifiable amorphous phase it is less useful in assessing the behavior of drawn highly crystalline polymers. At least two recent reports suggest that the origin of the retraction tendency may be the deformed lamellar crystals (1, 2). Because the lamellar polymer crystals are small, there is a large amount of crystal surface or crystal interface. Deformation of the crystals increases the surface or interface area thus increasing the free energy of the system and creating the driving force for retraction. This paper reports on experiments performed to obtain a measure of the role of crystal size and crystallinity in the retraction of polyethylene.

SAMPLE CRYSTALLIZATION

Marlex 6050, a linear polyethylene produced by Phillips Petroleum Company was used throughout this study. As part of a previous study (3) using the same lot of polymer, molecular weight determinations were made with the results $\bar{M}n$ = 5500 and $\bar{M}w$ = 92,500. Sheet specimens 4 mm thick were prepared by pressing pellets of

Marlex 6050 in a rectangular mold at 150 C and 130 kg/cm^2. The sheets were then heated to 180 C for 75 minutes and pressed to a thickness of 3.2 mm. At the end of the 75 minutes, the molds were transferred to a silicone oil bath preset to the desired crystallization temperature. After the desired time for crystallization, the mold was quenched by immersion in ice water. Table 1 summarizes data on the crystallization conditions and characterizations of the specimens by density gradient column and small angle Xray diffraction. The SAX data were obtained on a Bonse and Hart type unit. The diffraction scans, after subtraction of diffuse scatter following the procedure of Muzzy (4), are reproduced in Fig. 1. These procedures yielded one set of four specimens with essentially the same density but differing in SAX spacing or lamellar thickness and another set of four specimens with the same SAX spacing but different densities. One specimen was prepared by quenching the mold from 180 C into ice water.

COLD DRAWING OF SAMPLES

High density polyethylene which has been crystallized relatively slowly at high temperatures is difficult to cold-draw in tension; it tends to fracture. For this reason, and because it permits direct control of the strain or draw ratio, a simple shear deformation was used. The sample geometry and the jaws used to perform the shearing is shown in Fig. 2. This apparatus was developed by Sternstein, Ongchin and Silverman and has been described in detail by them (5). For cold drawing, a sample sheet was machined to the shape shown on the left of Fig. 2. The actual sample section dimensions were 4.76 mm wide, 1.52 mm thick and 7 mm long. The shearing was done in an Instron tester by moving the U-shaped jaw while holding the center section

TABLE 1

SAMPLE CHARACTERIZATIONS

Crystallization Temperature	Crystallization Time, Hours	Density gm/cm^3 at 23 C	Density* % Crystallinity	SAX Spacing, Å	SAX Peak** Width (minutes)
127	10	0.975	80.0	530	5.6
125	3	.974	79.4	450	7.2
123	20	.976	80.5	420	8.9
121	20	.975	80.0	390	9.8
127	5	.970	77.3	530	5.6
127	3	.968	76.2	530	5.6
127	1	.963	73.5	530	5.6
Quenched	--	--	68.6	240	18.2

*Based on ideal crystal and amorphous densities of 1.011 gm/cm^3 and 0.852 gm/cm^3 at 23 C.

**Measured at half maximum intensity

stationary. A progression rate of 0.5 cm/min (strain rate of 1.05 min^{-1}) at a temperature of 60C was used throughout. All specimens were deformed to a total nominal strain (total progression divided by gap width) of 4.0 or a "draw-ratio" of 5.0. When the deformation reached this point the sample was unloaded. A typical stress-strain curve for the simple shear deformation is shown in Fig. 3. Table 2 summarizes data on the maximum stress and the stress at maximum strain for each sample.

RESULTS - RETRACTION MEASUREMENTS

Observations to characterize the retraction tendencies of the samples were made in relaxation and creep type testers. The relaxation tester was fitted with jaws similar to those used for the original shearing. Samples which had been strained or cold drawn at 60 C as described above were clamped in this apparatus at room temperature and the jaws constrained against any sample motion. The assembly was then plunged into a silicone oil bath pre-set to the desired test temperature and the stress required to keep the sample from retracting was recorded as a function of time. The creep type tests were similarly performed except that change in sample strain was permitted under constant load or stress.

The results of the relaxation-type tests are summarized in Fig. 4 and 5 showing the retractive stresses developed at temperatures of 70 C and 100 C respectively. The retraction, under zero load, measured in the creep tests is likewise summarized in Figs. 6 and 7.

For the set of samples crystallized at different temperatures the essential difference in structure is the lamellar thickness, or the amount of lamellar fold

TABLE 2

STRESSES RECORDED IN SIMPLE SHEAR DEFORMATION OF POLYETHYLENE SAMPLES

Crystallization Conditions Hours/Temperature	Maximum Observed Stress, Dynes/cm^2	Stress at Maximum Strain Dynes/cm^2
10/127 C	13.9×10^7	9.40×10^7
3/125	12.9	9.96
20/123	12.9	9.68
20/121	13.0	9.59
5/127	13.0	9.26
3/127	12.2	8.83
1/127	10.9	8.18

surface. If, as has been hypothesized (1, 2) the deformation expands these surfaces or increases the total free energy associated with them, then the samples with the smaller lamellar spacings having the larger amount of surface per unit volume should have the greater tendency to retract. The data summarized at the top of Figs. 4, 5, 6 and 7 would appear to support this hypothesis. In all cases the samples with the smaller lamellar spacings developed the larger retractive stresses or retracted more rapidly. Estimating that the surface or interface area in each sample is inversely proportional to the lamellar thickness or to the SAX spacing, the above hypothesis predicts that the retractive force should be inversely proportional to the SAX spacing. The figures in Table 3 are in reasonable agreement with this considering the uncertainties in making a direct relationship between SAX spacing and crystal surface per unit volume.

The data recorded at the bottoms of Figs. 4, 5, 6 and 7 compare specimens which were all crystallized at the same temperature (127 C) but for different lengths of time so that the densities or "crystallinities" are different. If the amount of crystal surface per unit volume increases with the crystallinity then, again following the above hypothesis, the higher density samples should show the greater tendency to retract. The data, however, indicate just the opposite.

These simple comparisons are, of course, vulnerable to the presence of other differences between samples than the lamellar thickness and "crystallinity" that are being cited as the pertinent parameters between experiments. The influence of varying crystallization temperature and time on other morphological parameters such as interlamellar links and networks is difficult to assess and could markedly influence the course of the deformation and testing. Light microscopy, replica

TABLE 3

COMPARISON OF RETRACTIVE FORCES AND SAX SPACINGS

Crystallization Conditions Hours/Temperature	SAX Spacing Angstroms	Retractive Stress Dynes/cm^2 x 10^{-6}	Stress Multiplied by SAX Spacing
10/127 C	530	9.3 at 70 C	4920
3/125 C	450	11.0 " " "	4950
20/121 C	390	11.5 " " "	4480
10/127 C	530	11.1 at 100 C	5880
3/125 C	450	11.7 " "	5270
20/121 C	390	12.2 " "	4770

electron microscopy and scanning electron microscopy observations were made and revealed no differences among the samples except for the one prepared by quenching the mold from the melt temperature. Sections of the quenched sample when viewed between crossed polars showed ringed spherulites 30μ in diameter with a 2μ ring spacing. The other samples were also composed of 30μ spherulites but no rings were evident. More directly important is the state of the specimens after cold drawing as that is the state in which the retraction characterizations were made and compared.

The simple shear cold drawing was carried to a maximum strain of 4.0 and upon removal of the drawing stress the specimens retracted to a strain of 3.4. They were then cooled to room temperature and no measurable change in strain occurred while specimens were held at room temperature. Characterizations of the orientation in this drawn state were made by wide and small angle Xray scattering. The procedures and results are discussed in a following section. The Xray characterizations confirmed that the set of samples crystallized at different temperatures to the same final density achieved the same state of orientation. This tends to confirm that the differences in retraction behavior in these samples is, as hypothesized, due to the differences in lamellar thickness.

The set of samples all crystallized at 127 C for different times to different final densities did not, however, achieve the same orientation on drawing. Lower density samples became more highly oriented than higher density samples. To ascertain the effect of orientation differences on the retraction behavior, one sample of material which had been crystallized at 127 C for 10 hours was sheared to a maximum strain of 4.5 where it achieved the same state of orientation as a sample crystallized at 127 C for 1 hour and sheared to a maximum strain of 4.0 (More detail of this comparison is given in a following section on the Xray characterizations.) A free

retraction experiment on this specimen showed it to retract more rapidly than the lower density specimen (Fig. 8). This is in agreement with our hypothesis and contrary to the apparent implications of the data at the bottoms of Figs. 4, 5, 6 and 7, which are due to the difference in state of orientation of the specimens. Also consistent with this are the facts that the quenched sample became more highly oriented than any of the others during drawing and exhibited the most rapid free retraction.

Thus, it appears that all of the data recorded on retractive forces and free retraction are consistent with the hypothesis. Still, some discussion of the retraction process itself is called for. In all of the free retraction experiments a rapid initial retraction occurred for the first few minutes followed by a slower continuing retraction which appears linear in relation to the logarithm of time. Similar behavior has been recorded for free retraction of tensile drawn polyethylene and polypropylene (2). In the retractive force measurements (relaxation type tests) at 70 C the force is observed to build up rapidly during the first few minutes and then approaches a value that appears stable. At 100 C, however, a maximum is observed in the retractive force at about 8 minutes followed by a decay or stress relaxation.

Following the conclusions of Stein (6, 7) based on his extensive characterization of the deformation of spherulitic polyethylene, this retraction behavior may be interpreted as follows: During the initial drawing two primary deformations occur; an interlamellar and/or interspherulitic mode and an intralamellar process. The first, which accounts for only a very small fraction of the total strain is rapidly and essentially completely recovered when the drawing load is removed. A part of the

intralamellar deformation is also recovered, that corresponding to the rapid retraction which would occur at 60 C, the drawing temperature. The measurement of retractive forces show a development of the retractive force during the first few minutes which is related to a retraction of the interlamellar deformation coupled to re-deformation or tightening of the intralamellar network. The longer-time decay of the retractive force at 100 C is attributed to interlamellar creep, leaving the question as to how near the potential retractive force is the observed maximum?

The data recorded in Fig. 9 show the results of relaxation tests on four oriented samples at 23, 50, 60 and 70 C, pre-loaded to a stress of 14.8×10^6 dynes/cm^2 at 23 C. This pre-loading should have oriented the interlamellar network. At 23 C only a relatively slow decay of the stress is observed. At 50 C and 60 C a rapid initial relaxation is observed which may be related to intralamellar orientation coupled with interlamellar disorientation until the stresses to balance the two modes is achieved. At 70 C further rapid intralamellar retraction is activated and so, following an initial stress decay, the stress is seen to rise and then stabilize. Because the specimens were originally drawn at 60 C, and because after removal of the drawing load both interlamellar an intralamellar retraction occurs, there is little or no driving force for intralamellar retraction activated in the tests at or below 60 C. While an apparently stable stress appeared to develop for the three higher temperature tests, the 23 C test did not stabilize probably due to much slower response at this lower temperature.

Figure 10 presents the results of a relaxation type test in which the stress was permitted to reach a stable value at 70 C before the temperature was decreased to

60 C for 60 minutes and then returned to 70 C. The stress followed this by decreasing when the temperature was lowered and returning to the same value when the temperature was returned to 70 C. A contrast is offered by the relaxation data obtained for a similar loading on undrawn specimens. As is seen in Fig. 11, the stress quickly decays to values much smaller than for the oriented specimens and continues to decay with time. The decay is more rapid at 100 C than at 70 C. From the shape of the original cold drawing curves it is estimated that at the stresses encountered in these tests, the induced interlamellar deformation accounts for no more than three percent strain. Comparing this to the difference between samples drawn to different extents leads to an estimate that the partial relaxation of the intralamellar orientation to affect the interlamellar network tightening in the retractive force measurement tests would cause only a few percent decrease in the measured potential retractive force. It is, therefore, concluded that the stable stress values recorded in the 70 C tests are a true measure of the potential retractive force within a few percent. The evident relaxation occurring within the experimental time scale leaves a larger uncertainty in the potentially achievable retractive force at 100 C. However, comparison of the data at 100 C to those at 70 C and of the temperature cycled force measurement (Fig. 10) establishes the positive sign of the temperature coefficient of the force. The hypothesis that the retractive force is related to crystal surface or interface free energy is not inconsistent with this. The deformation changes both the interface area and the character of the interface. The fold surface, for example, becomes larger but its orientation with respect to the unit cell changes. We may interpret the positive temperature coefficient as indicating that deformed interface has a lower entropy than the undeformed interface.

CHARACTERIZATION OF ORIENTED STRUCTURE

Most of the research on cold-drawing of crystalline polymers has used a tensile extension to deform and orient the sample. As noted previously, Stein (6, 7) has shown that the mechanical response can be interpreted in terms of an essentially elastic interlamellar/interspherulitic deformation with a very rapid response in series with a slower intralamellar deformation. Probably the most extensive studies of the structural character of the deformation have been made by Peterlin and his colleagues. A recent paper presents specific results on cold drawing of high density polyethylene (8). Peterlin's interpretation has the drawing process begin with lamellar rotation and reorientation (interlamellar deformation) followed by slip and tilting of molecules within lamellae (intralamellar deformation) and eventually breaking of lamellae to form new fibrils. Work in this laboratory (9) on tensile drawing of rods of high density polyethylene (similar to that used in this study) is in agreement with Peterlin's model but suggests that while the lamellae deform relatively little breaking up occurs until the draw ratio exceeds 4 or 5.

The simple shear deformation differs from tensile drawing in two primary features of concern here. One, the symmetry of the orientation which results is different. Two, the dilatational stress influences may be different in that a tensile drawn sample is more free to expand (decrease in density) than is a simple shear specimen. An affine, constant volume, tensile deformation of a sphere produces an ellipsoid with circular symmetry about the extension axis. An ideal, constant volume simple shear deformation of a sphere proceeds as indicated in Fig. 12. The plane of maximum strain starts out at 45^{0} to the plane of the applied shear stress and rotates with increasing strain toward a direction parallel to the plane of the applied

shear stress. In the plane of maximum strain, which expands in area, the circular section of a sphere grows in one direction while remaining of constant width in the other. The simple shear to strains of 4 as performed in this study are not expected to follow this ideal any more than a tensile drawing is expected to be affine and constant volume. However, examination of several specimens with wide and small angle Xrays from many directions consistently confirmed that the primary orientation direction was essentially coincident with the ideal plane of maximum deformation and the symmetry was as would be expected from this idealized picture.

Figure 13 presents two typical wide angle Xray patterns taken on a specimen crystallized for 10 hours at 127 C before and after cold-drawing. The Xray diffraction was done on a General Electric XRD-3 unit with a copper target. Further details of this apparatus and procedure have been described by Muzzy (4) and by Falender (10). Densitometer traces about the (200) and (110) rings indicate orientation of the drawn specimen in the direction expected based on the idealized picture of the simple shear deformation as may be seen from Fig. 14. There is some evidence of a second shoulder distorting the peak on the (200) ring trace. In the simple shear deformation the dilatational stress which develops is countered by a stress normal to the shear stress which arises because the sample is constrained in that direction (5). Applying modest tensile stress in this direction tended to decrease the shoulder suggesting that this stress may be the cause of the shoulder.

Unit cell or molecular orientation characterizations were made by measuring the widths of the (200) intensity traces at one half maximum intensity. These results, and some similar (110) characterizations are recorded in Table 4. Essentially

identical half widths were obtained for the samples which had been crystallized at different temperatures to the same final densities. However, for the series crystallized at 127 C for different times the half widths range from 59 to 74 degrees indicating greater orientation for the lower density samples. When the maximum shear on the 10 hour/ 127 C sample was increased from 4.0 to 4.5 the half width decreased from 81 to 72 degrees making it more comparable to the lower density samples. The quenched sample achieved the greatest orientation.

In Table 5 some wide angle orientation characterizations are recorded for specimens after free retraction and retractive force tests. When a sample is constrained and heated to 70 C in a retractive force test the width decreases from 81 degrees to 68 degrees indicating an improvement in orientation associated with the tightening or re-orientation of the interlamellar network. In a similar test at 100 C the widths after 700 minutes are as before the test. Presumably the re-orientation of the interlamellar network has been compensated by disorientation related to intralamellar relaxation which is reflected in the observed decay of the retractive force.

In the free retraction tests an improvement in orientation is also noted after 2 minutes at 100 C, but after 2000 minutes the orientation has decreased below that prior to the retraction. Again, during the initial period of rapid retraction the interlamellar network may re-orient more than compensating, temporarily, for the decreasing orientation associated with intralamellar retraction. In the longer run however, this orientation is lost. At 70 C, where the total retraction is less, there is evidence only of a small decrease in orientation. A comparison may also be made of the relative effects of free retraction at 100 C of samples originally crystallized 10 hours/127 C, 1 hour/127 C and 20 hours/121 C. The sample crystal-

TABLE 4

WIDE ANGLE XRAY DIFFRACTION

WIDTH OF 200 PEAK AT HALF MAXIMUM INTENSITY

IN SHEARED SPECIMENS

Sample Crystallization Hours/Temperature	Width of (200) Peak Degrees
10/127	81
3/125	81
20/123	81
20/121	78
5/127	74
3/127	74
1/127	59
Quenched	49
10/127*	72

*This specimen sheared to maximum strain of 4.5, all others sheared to maximum strain of 4.0.

TABLE 5

WIDE ANGLE XRAY DIFFRACTION ORIENTATION CHARACTERIZATION AFTER RETRACTION TESTS

TEST	Width at 1/2 Maximum Intensity Degrees (200)	(110)
None	81	103
Retractive Force Test, 2000 min. at 70C	68	93
700 min. at 100C	81	103
Free Retraction, 2000 min.at 70C	81	106
2000 min. at 100C	87	109
2 min. at 100C	62	
Free Retraction, 2000 min. at 100C*	81	
2000 min. at 100C**	87	

Samples were crystallized at 127 C for ten hours and sheared to a maximum strain of 4.0 at 60 C prior to mechanical tests except as marked by asterisks.

*This sample crystallized at 127 C for 1 hour

**This sample crystallized at 121 C for 20 hours

lized at 1 hour/127 C is of lower density, orients the most during cold drawing, retracts the most and shows the largest decrease in orientation, the (200) width increasing from 59 degrees to 81 degrees after 200 minutes free retraction at 100 C. The sample crystallized 20 hours/121 C has the same original density as the one crystallized 10 hours/127 C, appears slightly more oriented after drawing but disorients equivalently more during free retraction corresponding to the observed greater retraction.

Some small angle Xray scattering patterns were also obtained using the GE XRD-3 unit with a copper target and a Statton-Warhus type camera. Details of the apparatus and procedure have been described by Falender (10). Figure 15 presents two typical SAXS patterns obtained on sheared specimens. Again, these patterns are similar to patterns obtained from tensile drawn materials if the direction of maximum strain is compared to the draw axis in tension. One difference is some evidence of scattering along the vertical direction which is presumed due to the normal stress effect described above in reference to the wide angle pattern. Densitometer traces of the SAXS patterns were taken about an arbitrarily chosen circle corresponding to spacing of 175 Å. The width of the "equatorial" scattering peaks at one half maximum intensity were used in characterizing the relative lamellar orientations for a selected set of samples as recorded in Table 6. (The "equatorial" scattering is most probably due to oriented voids and dilations but the prior work of Muzzy (4) suggests that these form at lamellar boundaries and their orientation corresponds to the lamellar orientation). Both the sample crystallized 10 hrs./127 C and the one crystallized 20 hrs./ 121 C have the same 43 degree SAXS width after drawing, again confirming that the samples of similar density with different lamellar thicknesses achieved the same state of orientation after drawing. The lower density sample, crystallized 1 hour/127 C has a 68 degree width indicating lesser lamellar orientation. As the wide angle results

TABLE 6

SMALL ANGLE XRAY SCATTERING

Width of "Equatorial" Scattering Peak Measured at Half Maximum Intensity of Trace on Circle Corresponding to 175 Angstrom Spacing

Sample	Half Width, degrees
Crystallized 10 hrs./ 127 C, drawn	43
Crystallized 20 hrs./ 121 C, drawn	43
Crystallized 1 hr./ 127 C, drawn	68
Crystallized 10 hrs./ 127 C, drawn	
plus free retraction 2000 minutes at 70C	71
plus free retraction 2000 minutes at 100C	77
plus free retraction 2 minutes at 100C	74
plus relaxation test 2000 minutes at 70C	71
plus relaxation test 700 minutes at 100C	83
Crystallized 20 hrs./121 C, drawn	
plus free retraction 2000 minutes at 100C	93
Crystallized 1 hr./127 C, drawn	
plus free retraction 2000 minutes at 100C	93

indicated greater orientation on drawing for the lower density samples it appears that this occurs by intralamellar deformation coupled to lesser lamellar orientation The interpretation of the overall deformation as an interspherulitic/interlamellar mode coupled in series with an intralamellar mode is, of course, an oversimplification as to some degree there must also be a parallel coupling of the two modes. In both free retraction tests and retractive force (relaxation) tests lamellar disorientation is observed with the magnitude being larger at 100C than at 70C. In these, and the wide angle, characterizations of the specimens used for retractive force measurements the samples were cooled to room temperature and then removed from the jaws. It is possible that some further dis-orientation of these stressed samples occurred on unloading.

All of the samples used in this study, except for the "quenched" one had been crystallized relatively slowly at comparatively high temperatures. The significance of this may be seen in the density data recorded in Table 7. All samples decreased in density on drawing and increased in density (to near the original values) after creep or relaxation tests. The quenched sample, however, increased in density to a value higher than its original value. That an annealing or re-crystallization of this sample occurred was confirmed by annealing an undrawn, quenched sample at 100C and observing the same density increase.

CONCLUSIONS

The association of a retraction tendency or long range entropy elasticity with the surface free energy of deformed, oriented lamellar polyethylene crystals is confirmed by the results of this study. The deformation of a crystalline or semi-

TABLE 7

DENSITY CHARACTERIZATIONS

gms/cm^3 at 23C by density gradient column

Crystallization hours/temperature	10/127C	20/121C	1/127C	Quenched
Before Drawing	.975	.975	.963	.955
Drawn	.962	.967	.959	.956
Drawn plus free retraction at 100 C	.974	.975	.968	.966
Drawn plus relaxation test at 100 C	.972	.974	.967	--
Annealed undrawn at 100 C	.975	.975	.963	.967

crystalline polymer is a complex process of coupled deformations in different phases at several structural levels and is not yet completely understood. Undoubtedly there may be elastic effects associated with several modes. In materials with a significant amorphous fraction rubberlike elasticity associated with molecular orientation in the amorphous fraction should be expected. The specimens used in this study were deliberately chosen and prepared to emphasize effects associated with crystal phase deformation. The morphological parameters, lamellar thickness and density, were deliberately varied and the effects on the elastic response were consistent with the hypothesis.

ACKNOWLEDGMENTS

This research was supported by the U.S. Army Research Office-Durham, North Carolina. The experimental work was performed at Rensselaer Polytechnic Institute's Materials Research Center supported in part by the National Aeronautics and Space Administration.

This research was a part of the doctoral dissertation of James R. Falender.

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FIGURE CAPTIONS

FIGURE 1. SMALL ANGLE XRAY DIFFRACTION AFTER SUBTRACTION OF DIFFUSE SCATTER

FIGURE 2. DIAGRAM OF SAMPLE SHAPE AND SIMPLE SHEAR JAWS

FIGURE 3. TYPICAL STRESS-STRAIN CURVE FOR SIMPLE SHEAR OF POLYETHYLENE

FIGURE 4. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 70C

FIGURE 5. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 100C

FIGURE 6. RETRACTION IN CREEP TEST AT ZERO STRESS AT 70C

FIGURE 7. RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C

FIGURE 8. COMPARISON OF RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C FOR SAMPLE SHEARED TO DIFFERENT EXTENTS. BOTH SPECIMENS ORIGINALLY CRYSTALLIZED AT 127C FOR 10 HOURS

FIGURE 9. RELAXATION AT DIFFERENT TEMPERATURES FROM ORIGINAL STRESS OF 14.8×10^6 dynes/cm^2 IMPOSED AT 23C. SAMPLES ORIGINALLY CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C

FIGURE 10. RESPONSE OF RETRACTIVE STRESS IN RELAXATION EXPERIMENT TO CHANGES IN TEMPERATURE. SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C.

FIGURE 11. STRESS RELAXATION IN UNORIENTED SPECIMENS FROM ORIGINAL STRESS OF 14.8×10^6 dynes/cm^2 IMPOSED AT 23C.

FIGURE 12. DEFORMATION OF A SPHERICAL ELEMENT IN IDEALIZED SIMPLE SHEAR

FIGURE 13. XRAY DIFFRACTION PATTERN FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C (LEFT) AND AFTER SHEARING AT 60C TO A STRAIN OF 4.0 (RIGHT).

FIGURE 14. DENSITOMETER TRACE OF (200) RING FROM FIGURE 13 (RIGHT)

FIGURE 15. SMALL ANGLE XRAY SCATTERING DIAGRAM FROM SAMPLE CRYSTALLIZED 10 HOURS AT 127C AND SHEARED AT 60C TO STRAIN OF 4.0 (LEFT) AND DENSITOMETER TRACE AT 175 Å (RIGHT)

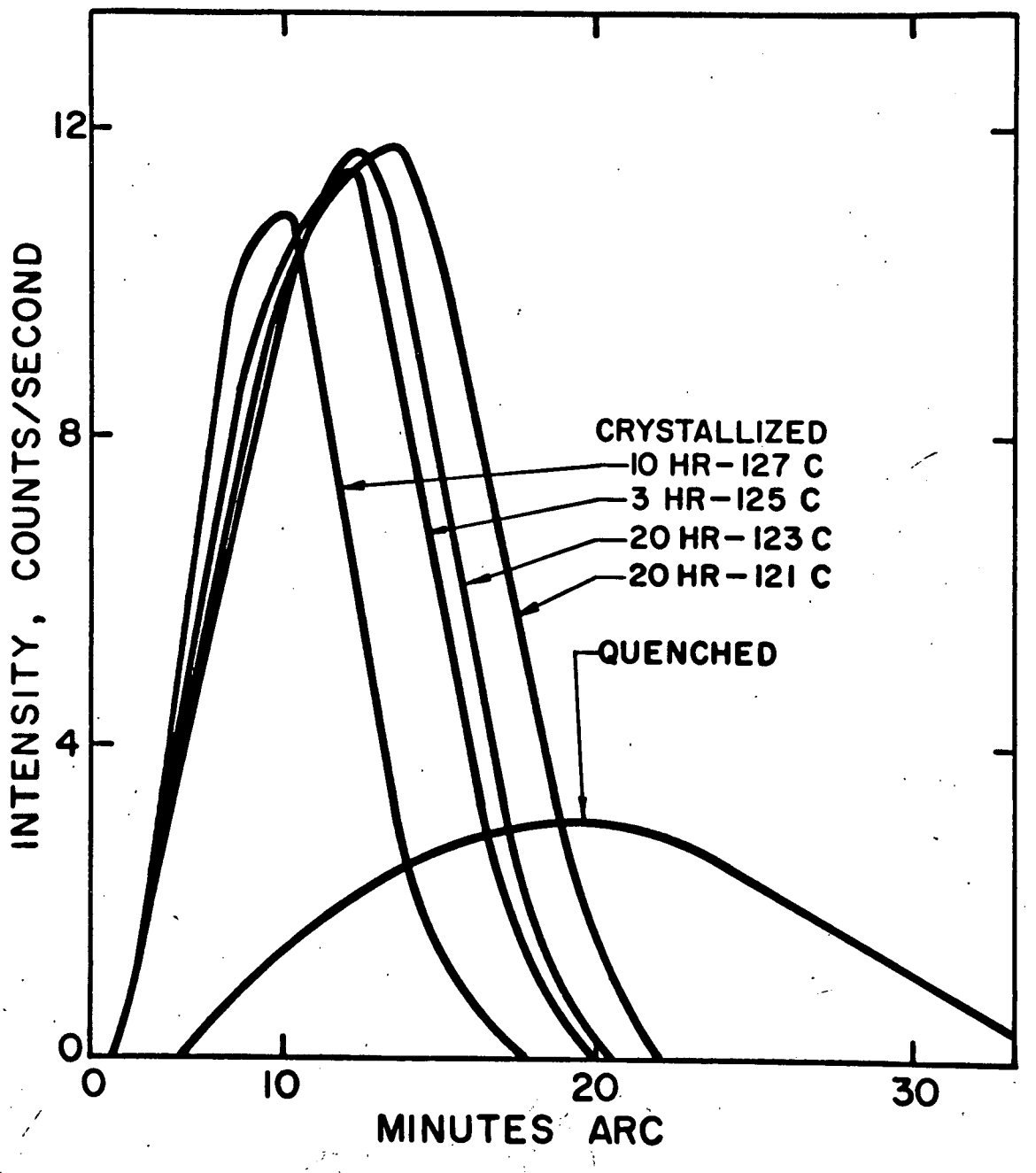


FIGURE 1. SMALL ANGLE XRAY DIFFRACTION AFTER SUBTRACTION OF DIFFUSE SCATTER

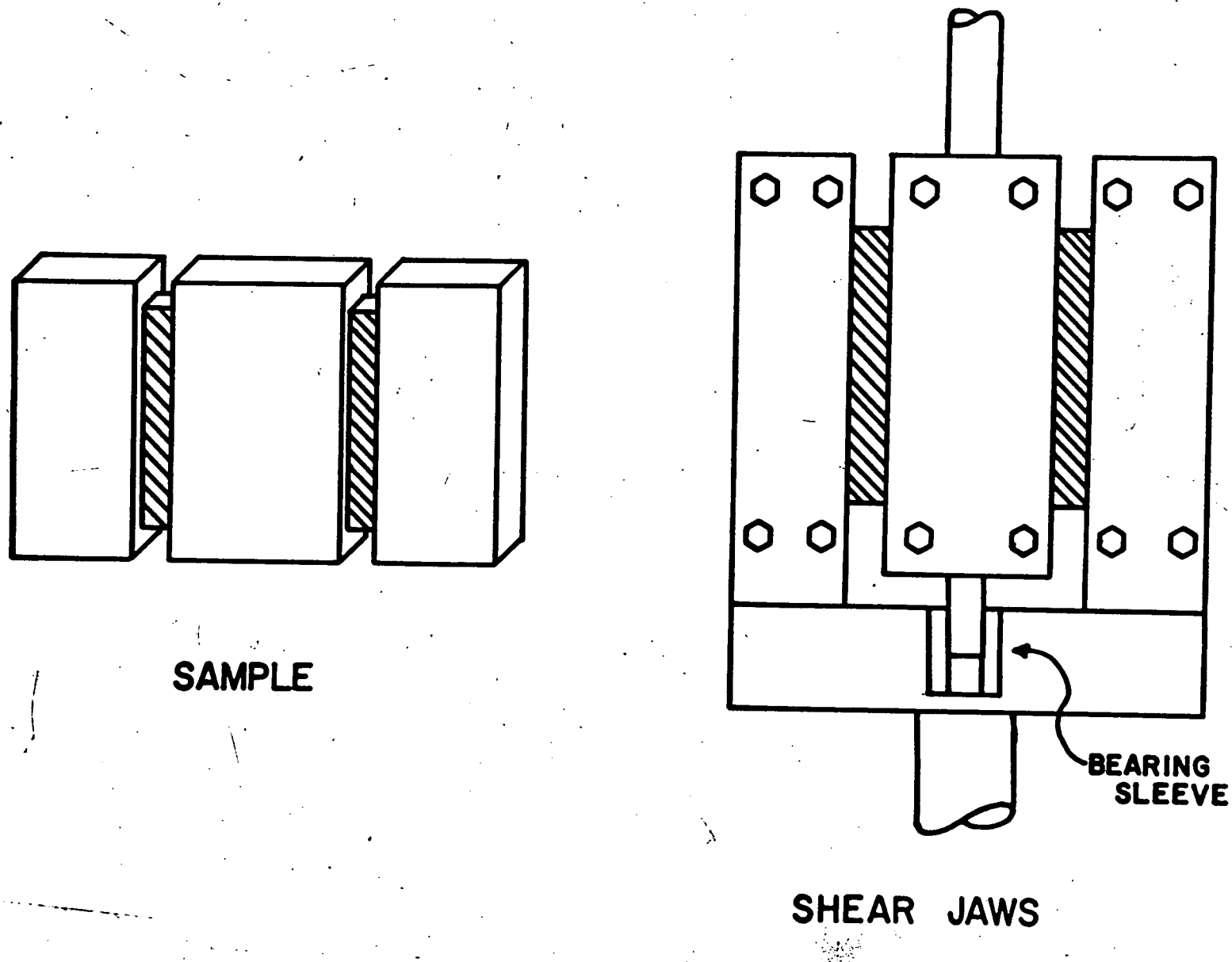


FIGURE 2. DIAGRAM OF SAMPLE SHAPE AND SIMPLE SHEAR JAWS

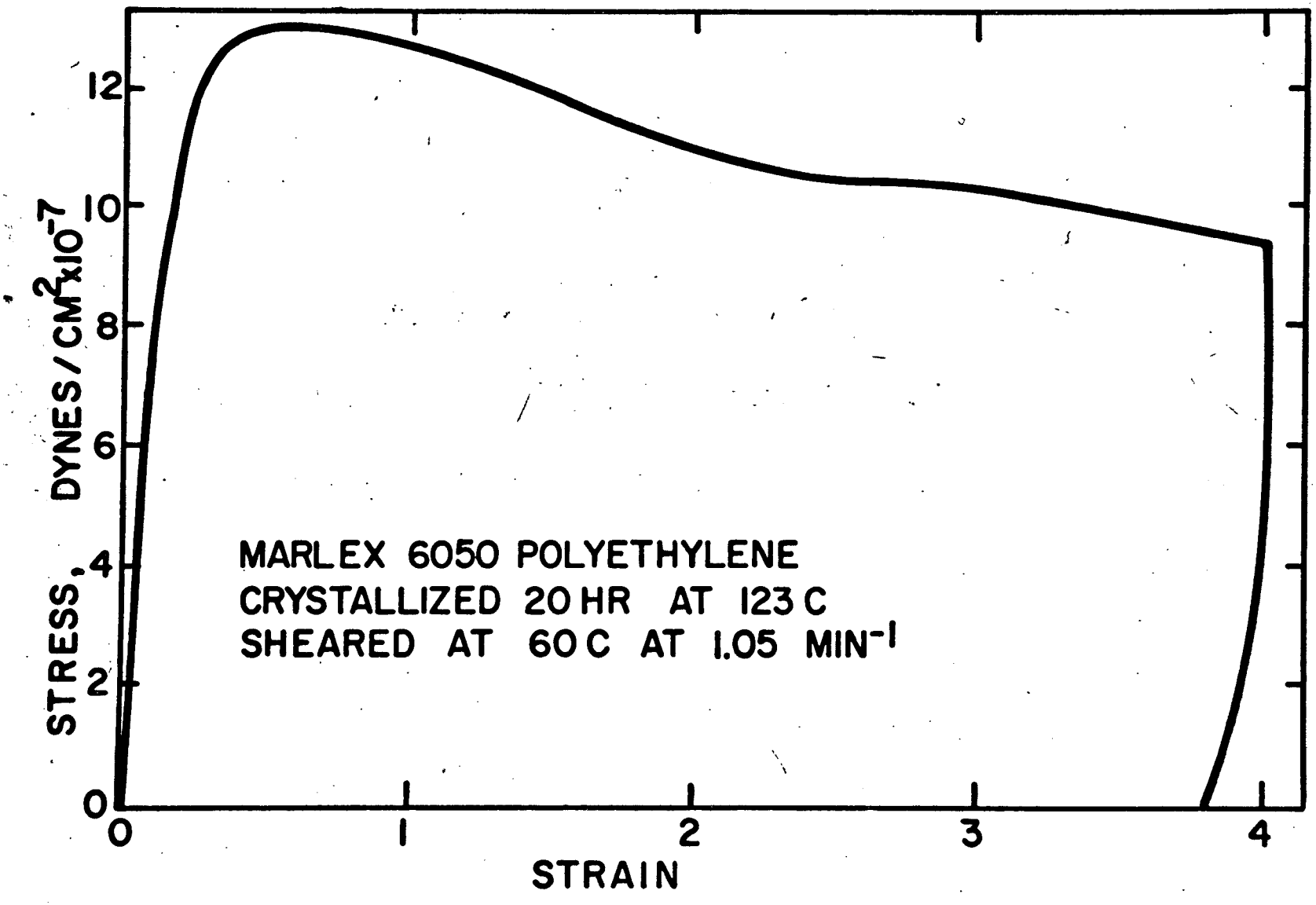
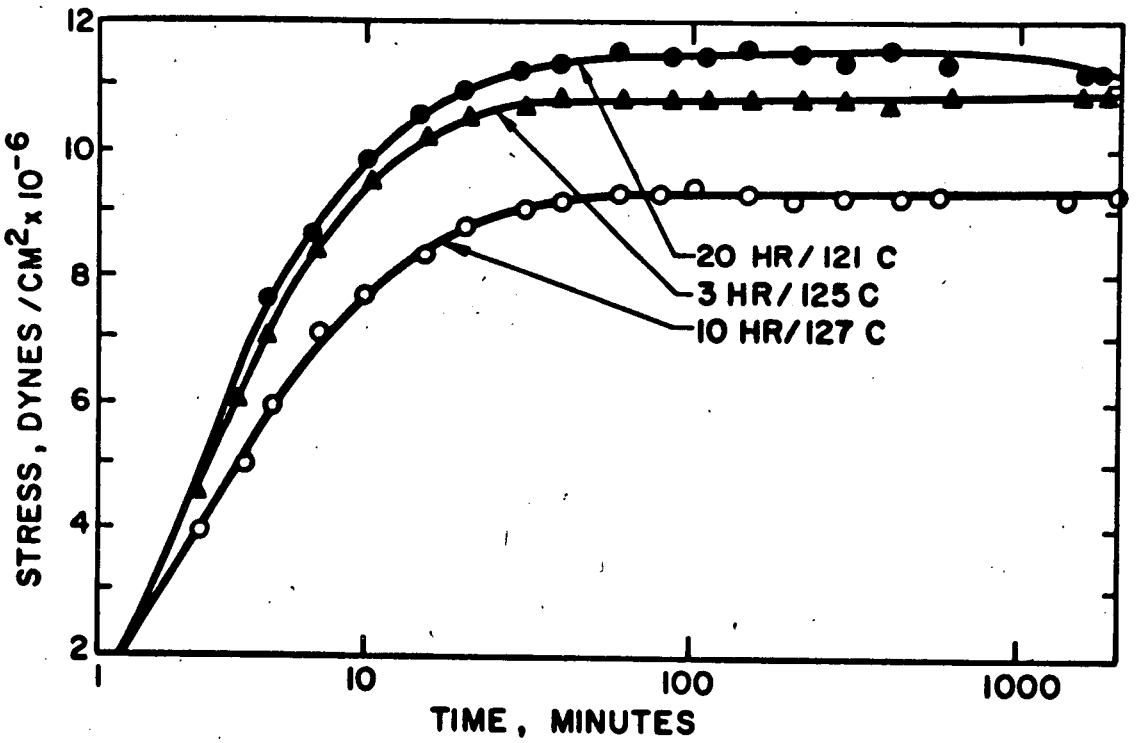


FIGURE 3. TYPICAL STRESS-STRAIN CURVE FOR SIMPLE SHEAR OF POLYETHYLENE



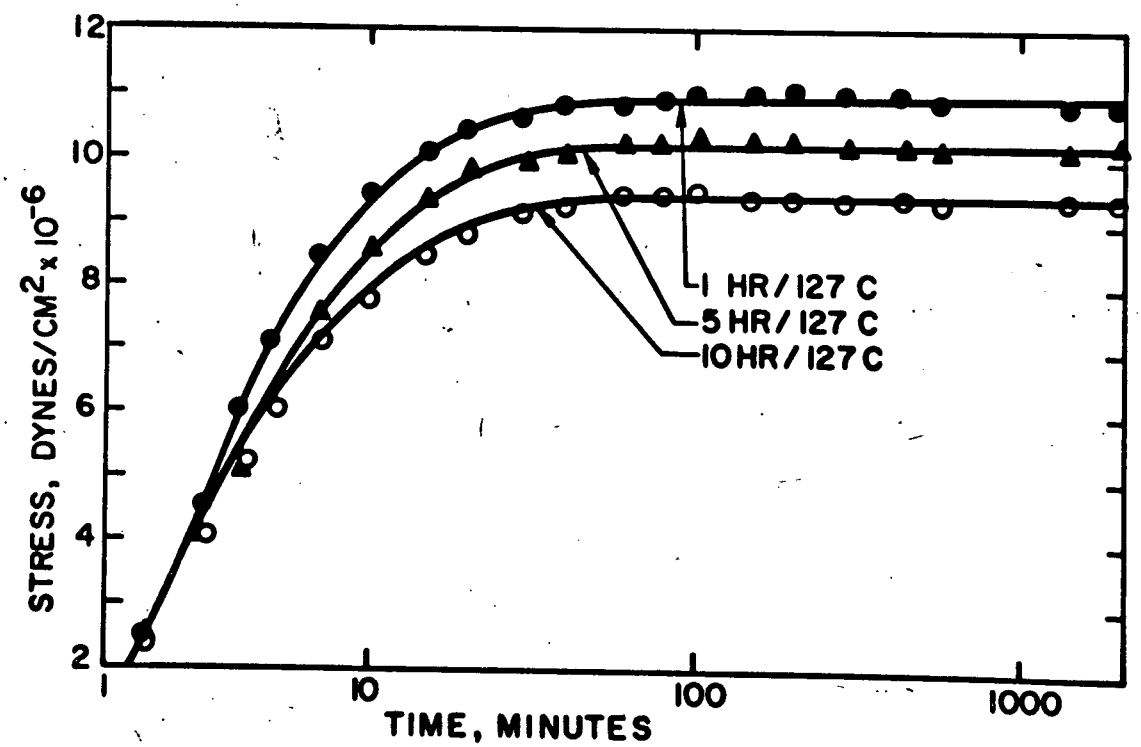
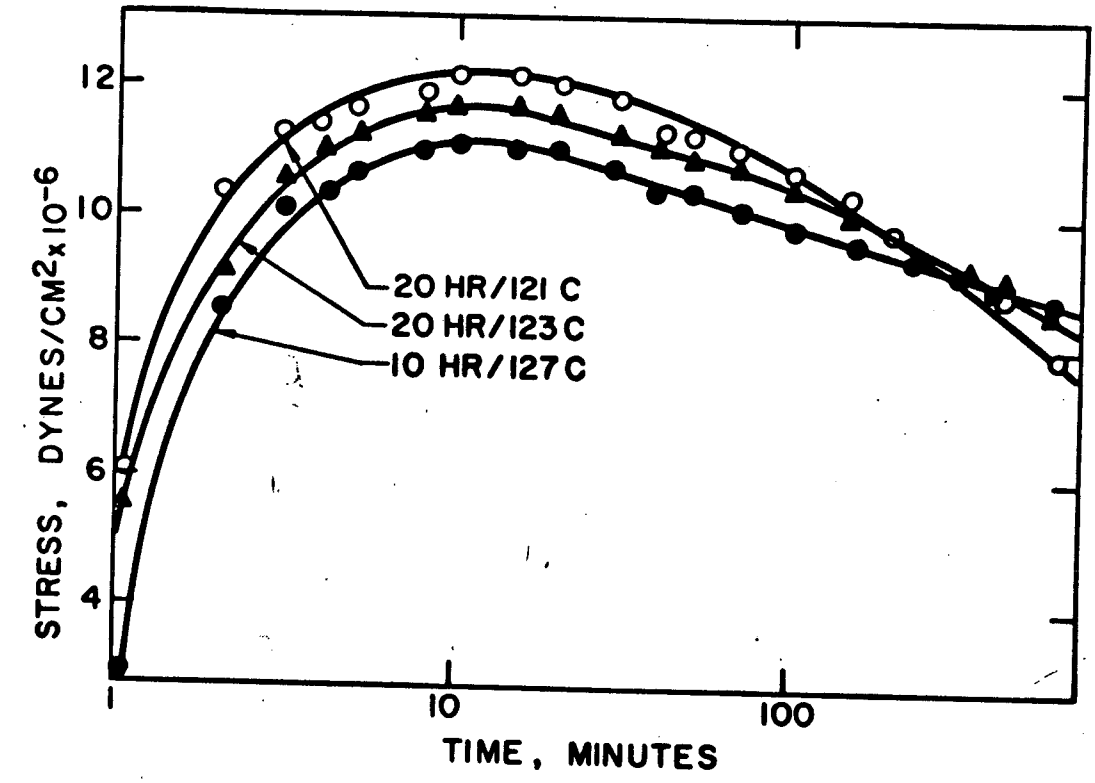


FIGURE 4. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 70C



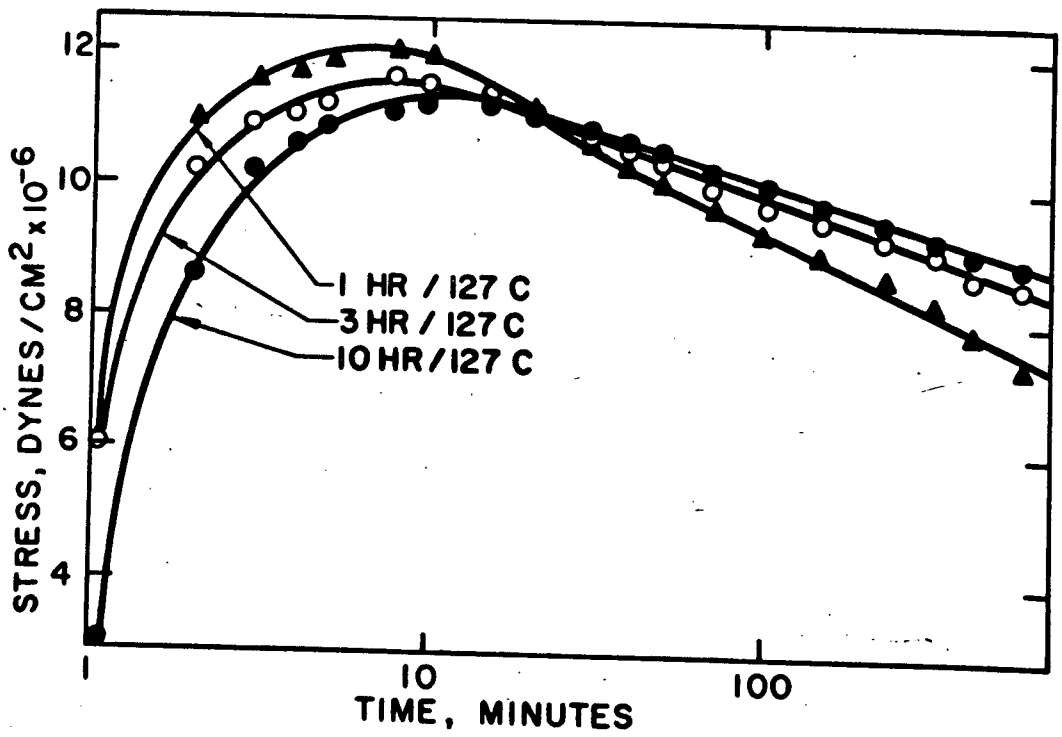
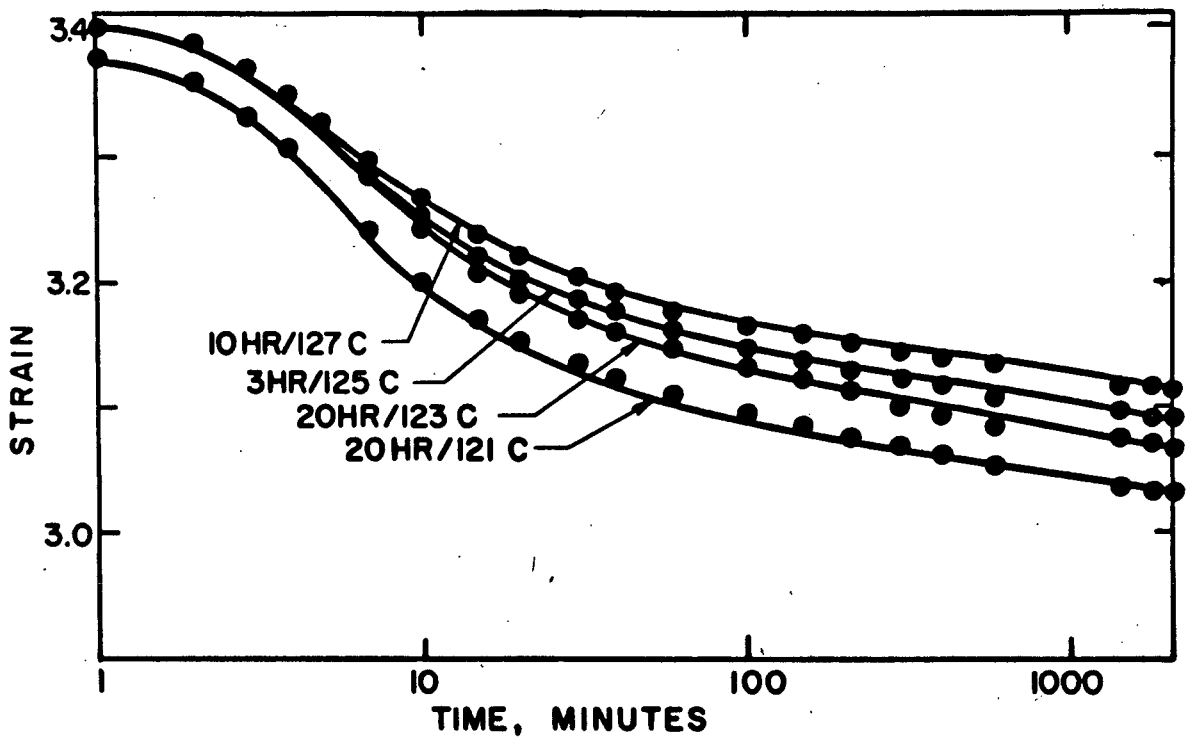


FIGURE 5. RETRACTIVE STRESS DEVELOPED IN RELAXATION TESTS AT 100C



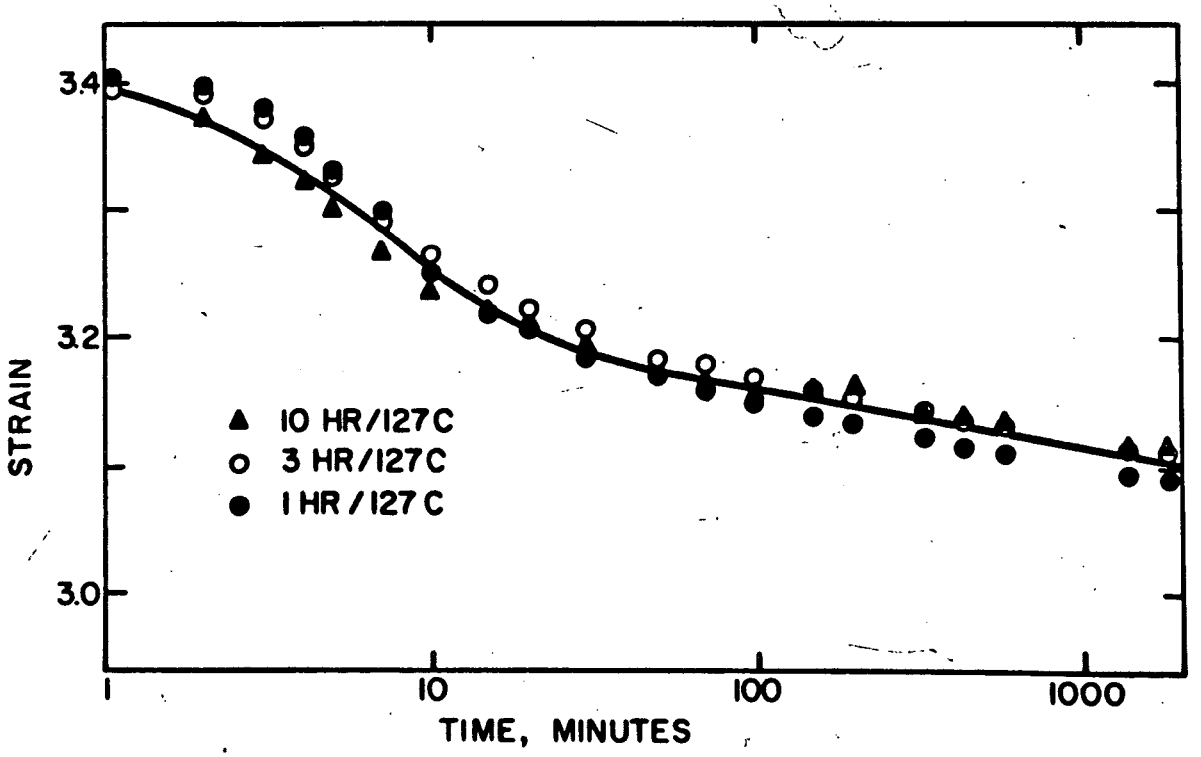
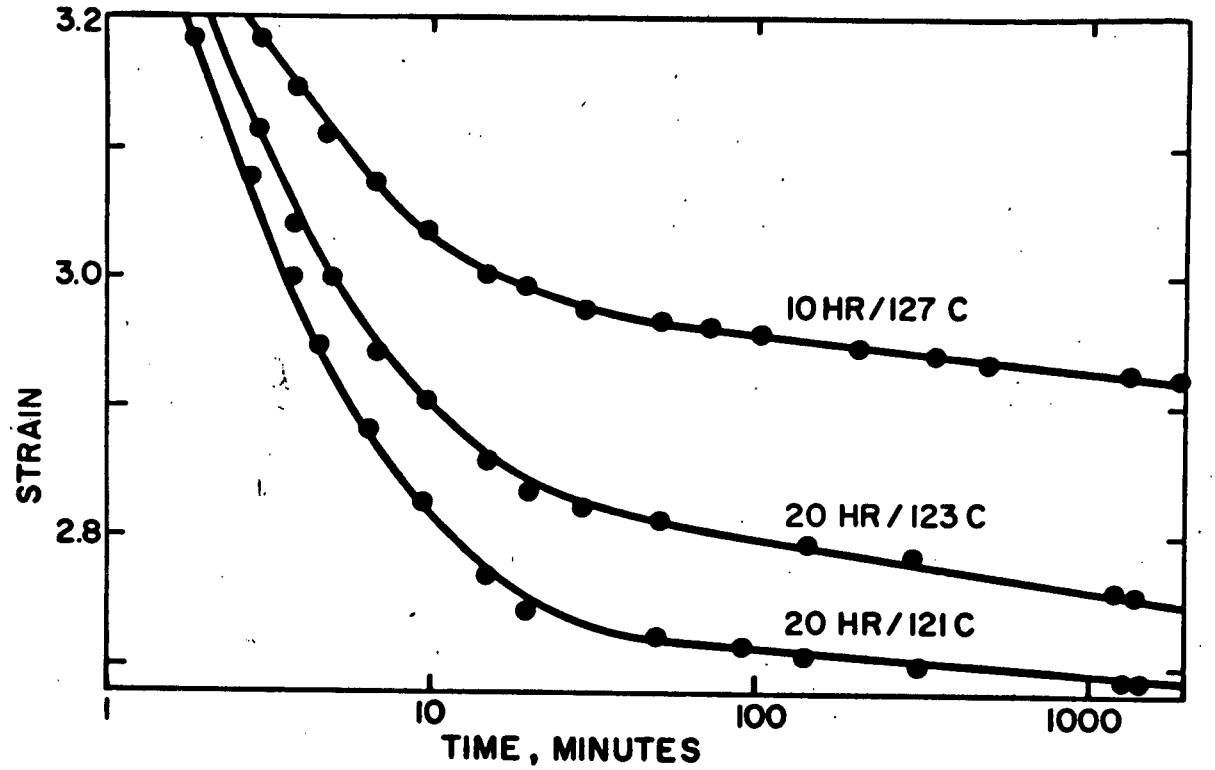


FIGURE 6. RETRACTION IN CREEP TEST AT ZERO STRESS AT 70C



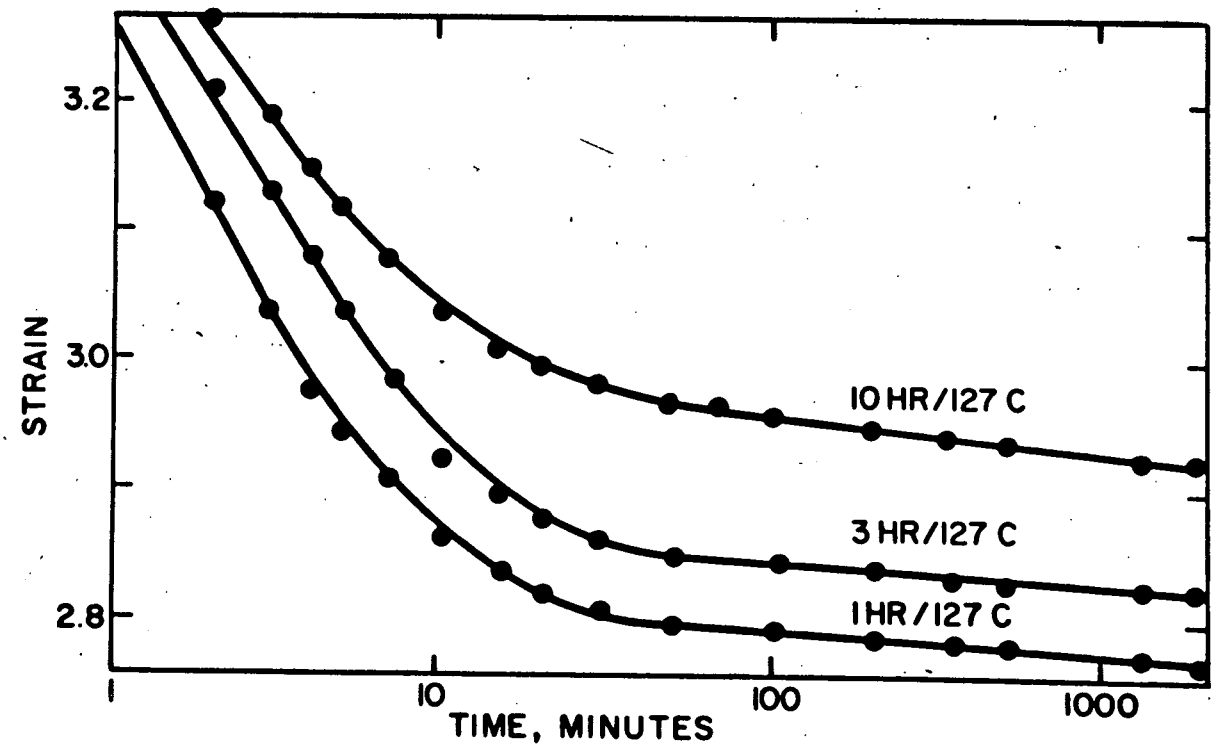


FIGURE 7. RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C

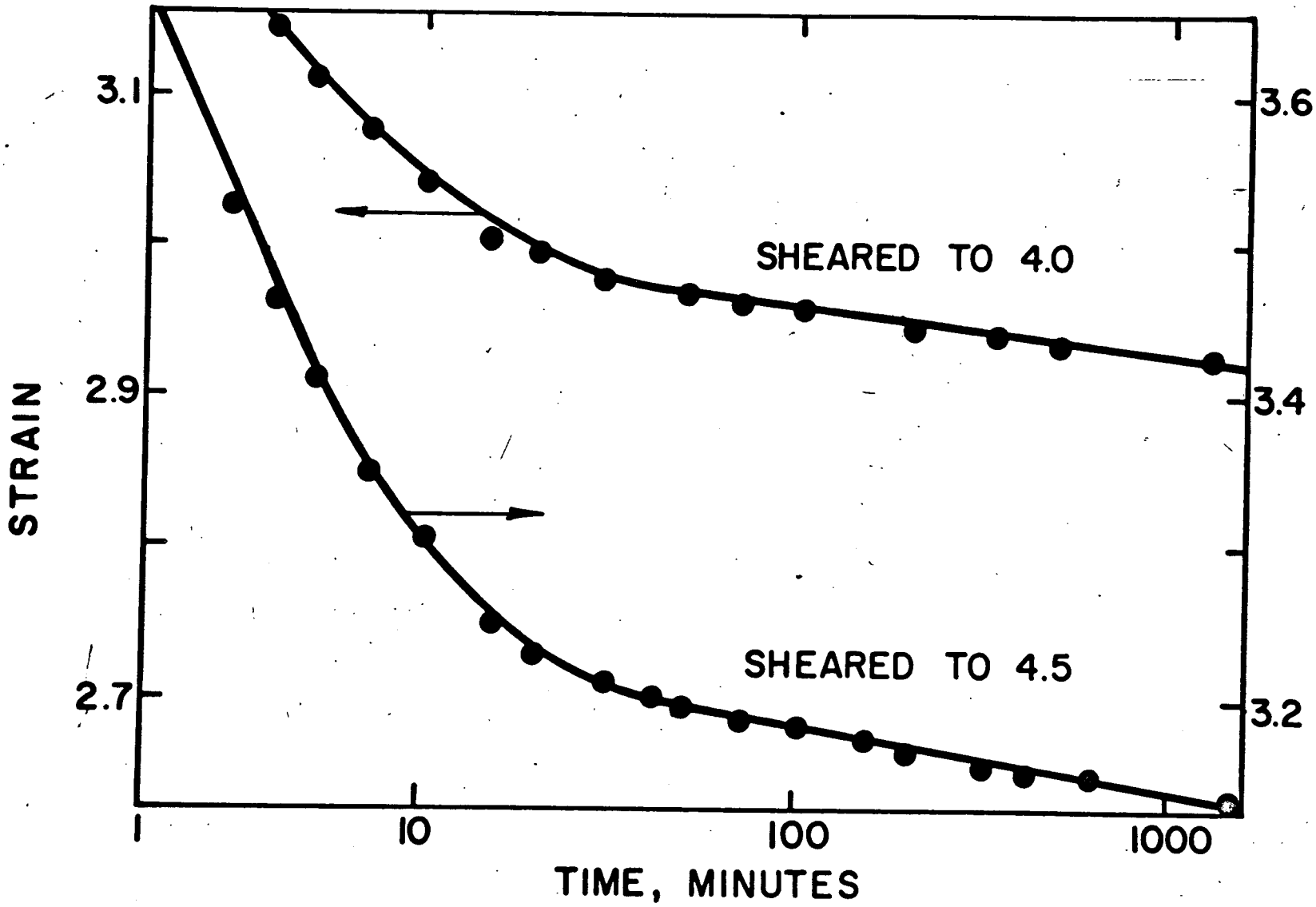


FIGURE 8. COMPARISON OF RETRACTION IN CREEP TEST AT ZERO STRESS AT 100C FOR SAMPLE SHEARED TO DIFFERENT EXTENTS. BOTH SPECIMENS ORIGINALLY CRYSTALLIZED AT 127C FOR 10 HOURS

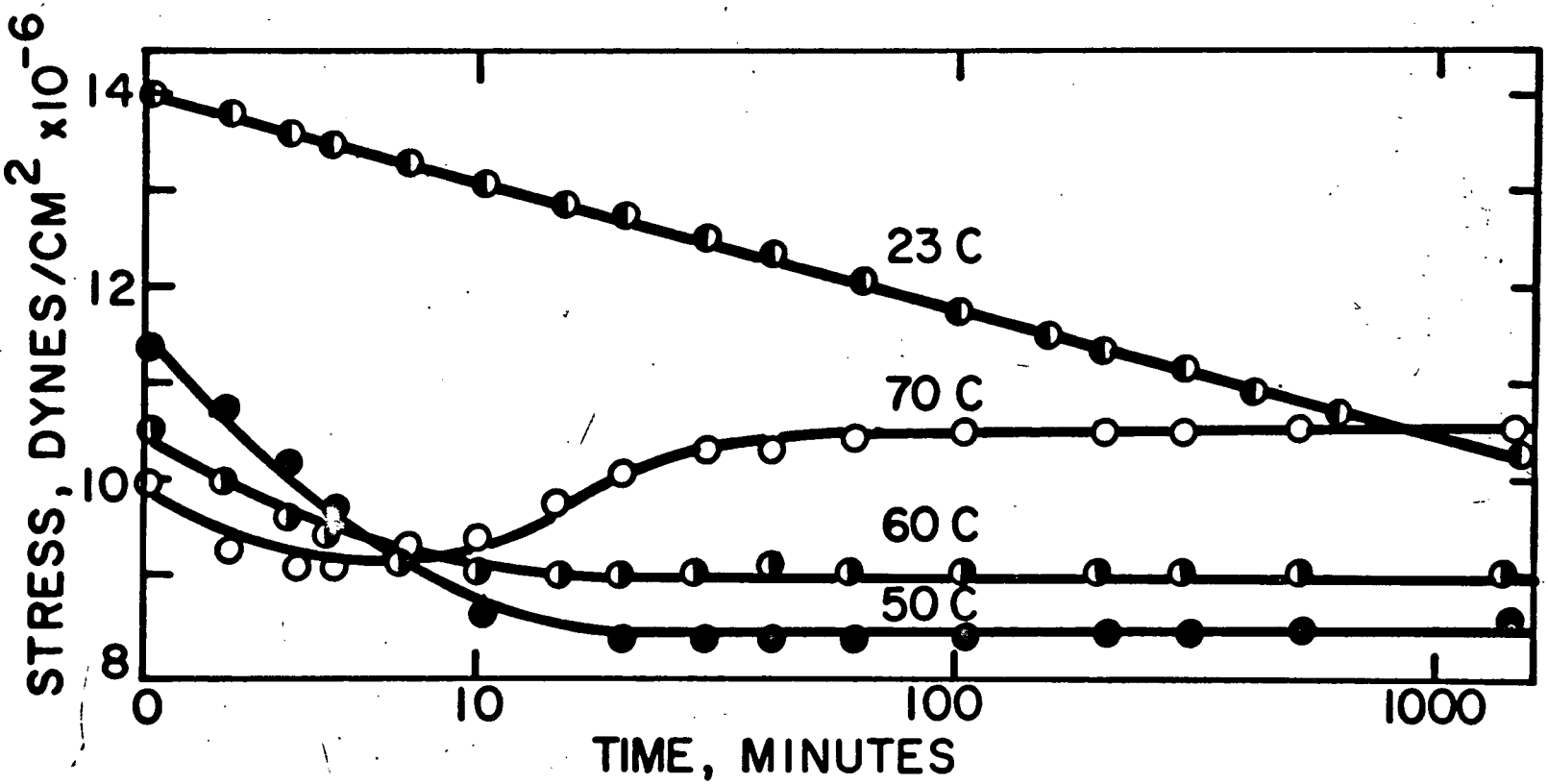
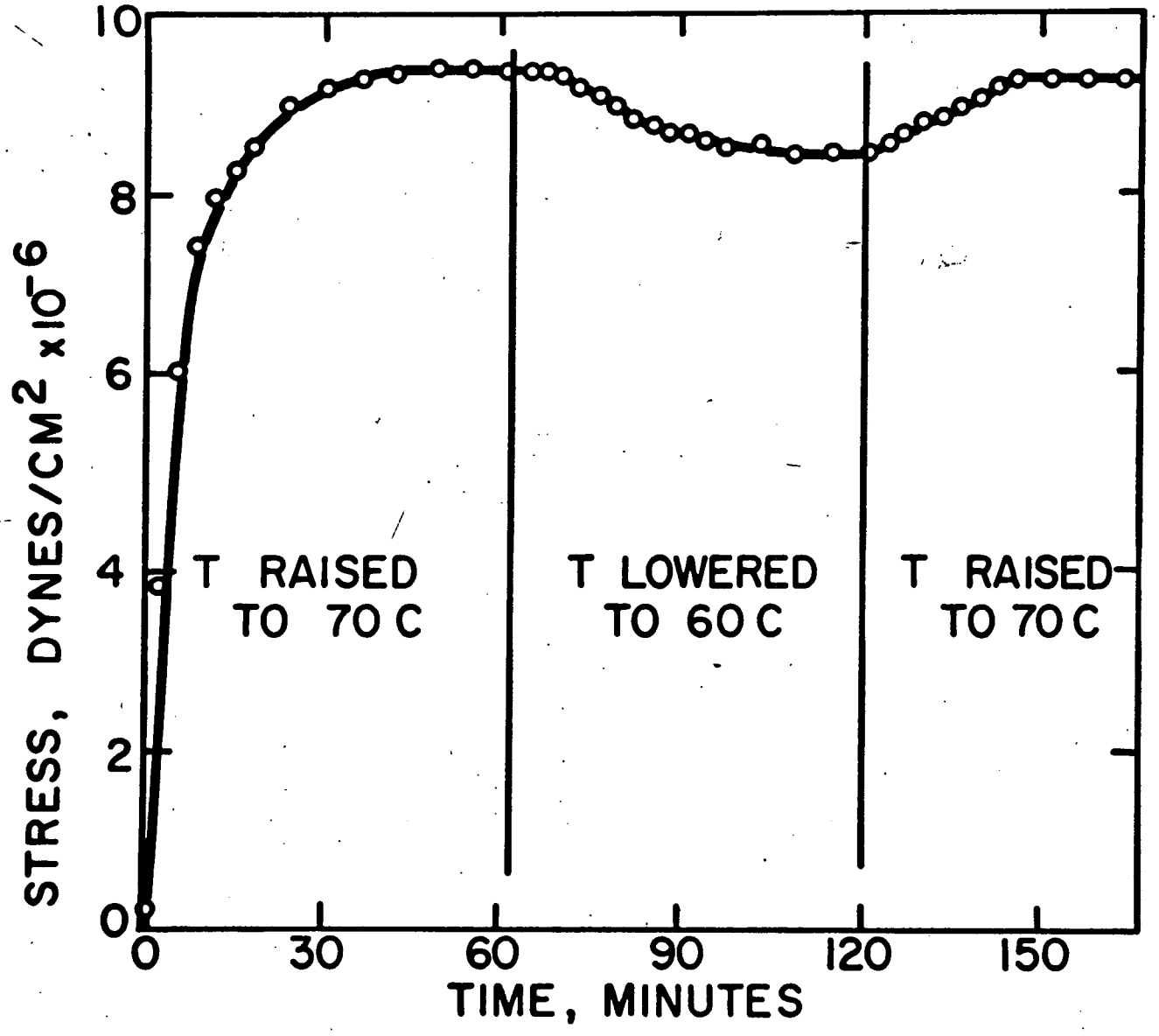


FIGURE 9. RELAXATION AT DIFFERENT TEMPERATURES FROM ORIGINAL STRESS OF 14.8 x 10^6 dynes/cm^2 IMPOSED AT 23C. SAMPLES ORIGINALLY CRYSTALLIZED 10 HOURS AT 127C AND SHEARED TO STRAIN OF 4.0 AT 60C



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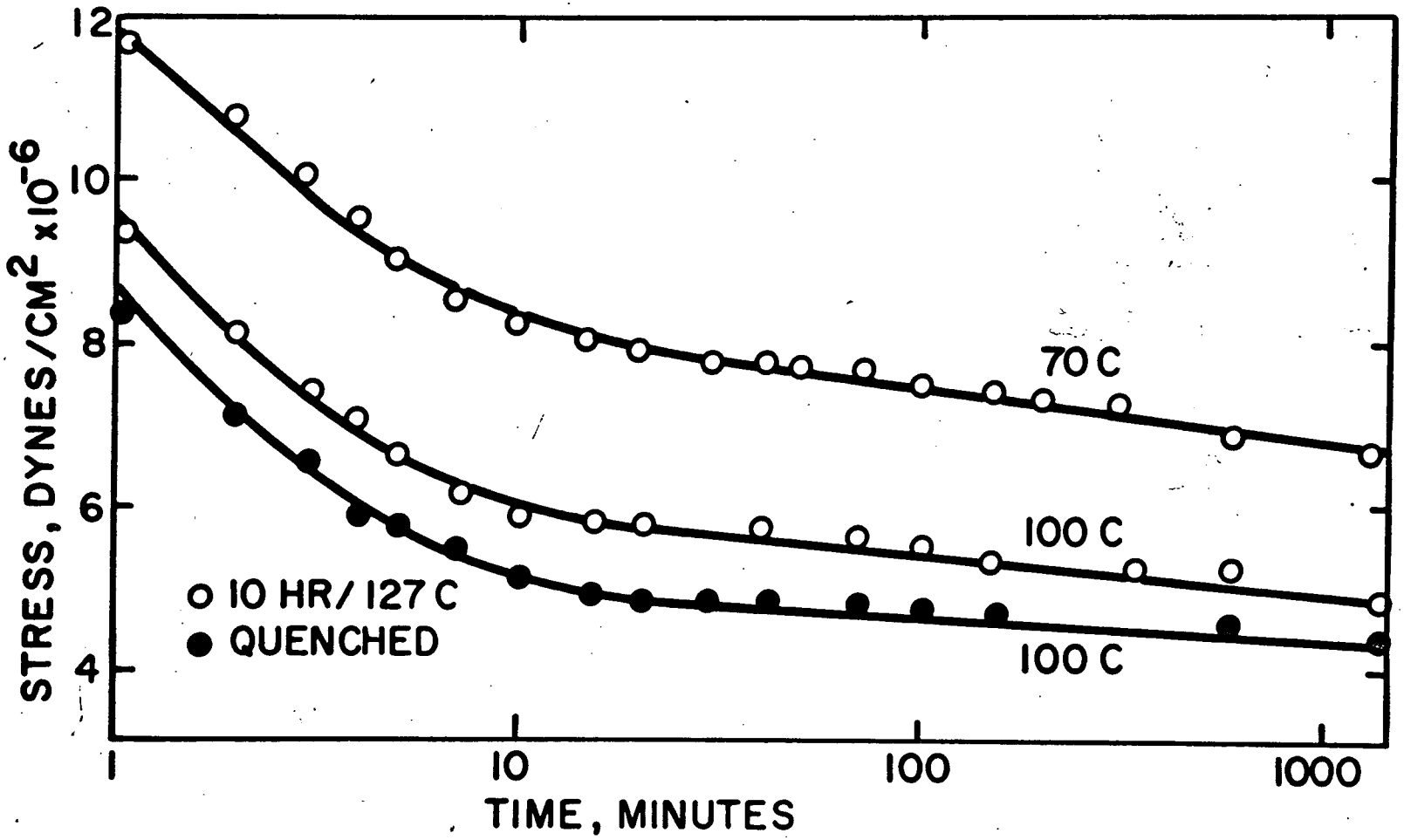

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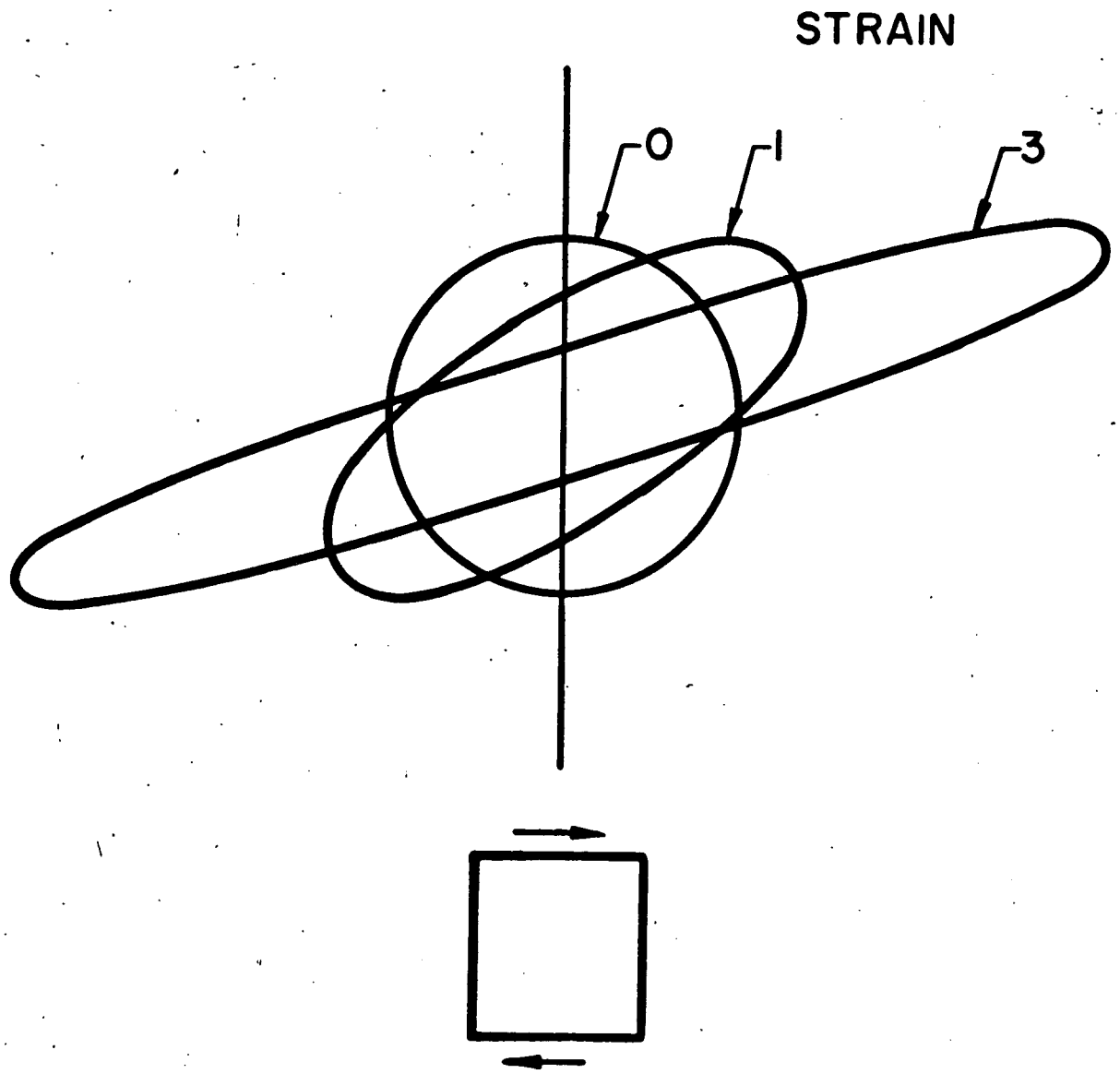

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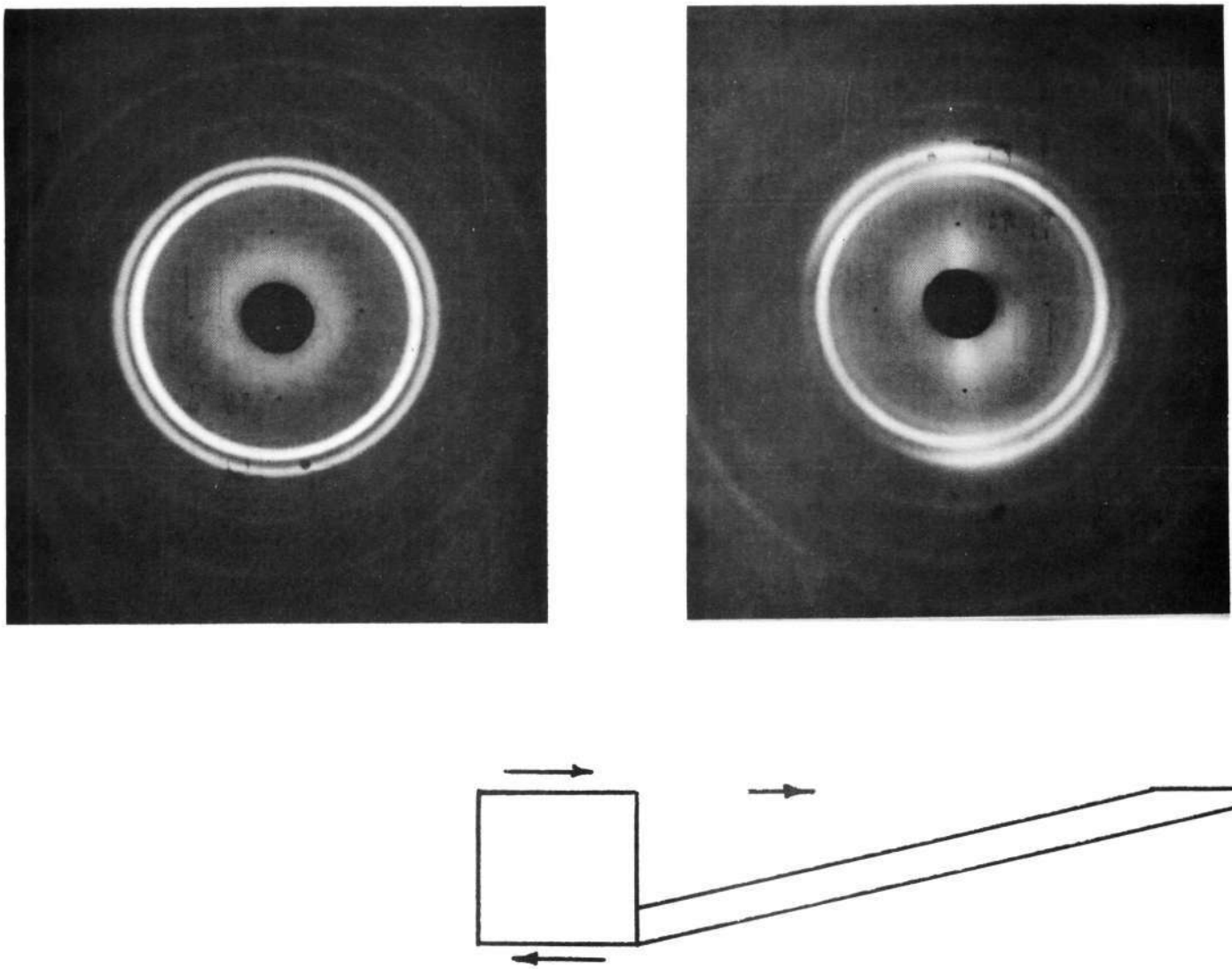

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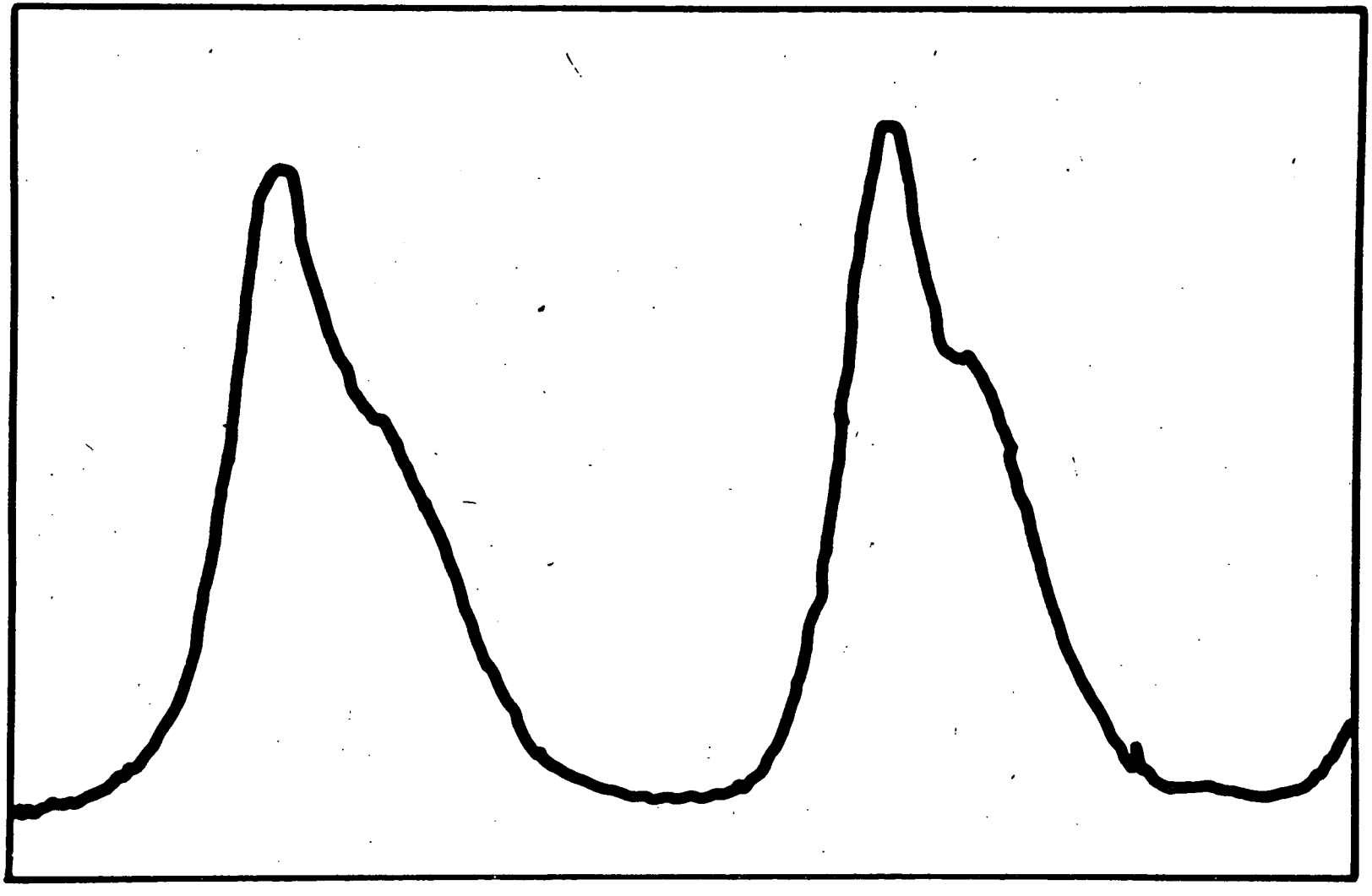
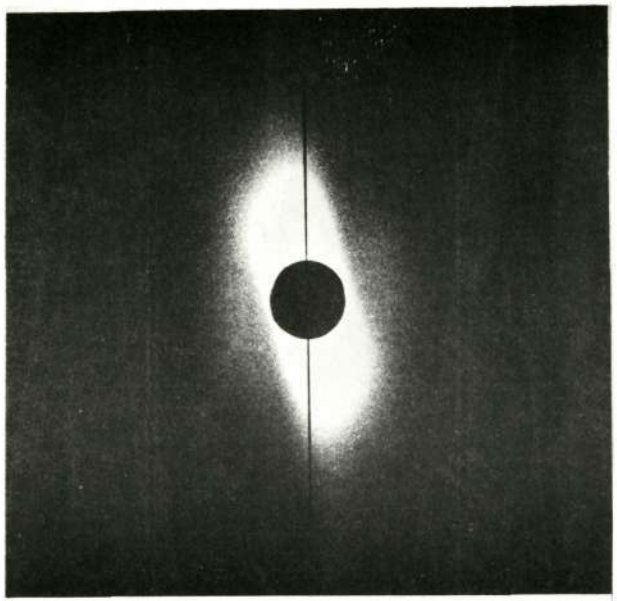
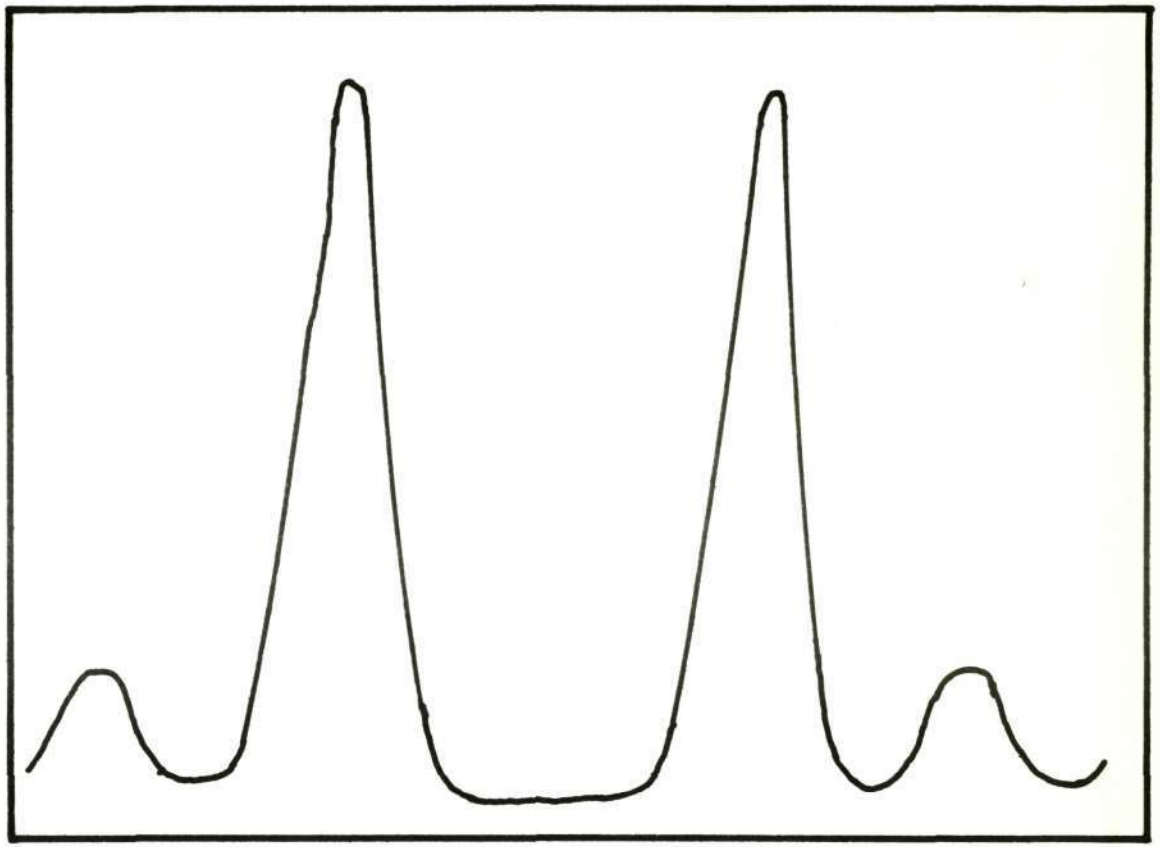


FIGURE 14. DENSITOMETER TRACE OF (200) RING FROM FIGURE 13 (RIGHT)





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